Vol. 16 MARCH • 1953 No. 1

LLOYDIA

A Quarterly Journal of Biological Science

Published by the Lloyd Library and Museum, Cincinnati, Ohio

The Influence of the pH Value of the Medium on the Availability to Plants of Iron and Manganese in Glass Frits[1]

ERLING REIN STROMME[2] AND F. L. WYND[3]

TABLE OF CONTENTS

[1]This report is the result of the efforts of several people. The following note of explanation is offered in order that the contribution of each may be recognized:

The project: All details of the project were planned cooperatively by Dr. G. H. McIntyre, Vice President in Charge of Research, Ferro Corporation, Charles A. Vana, Research Chemical Engineer, Ferro Corporation, and F. L. Wynd, Research Professor, Michigan State College.

The equipment: The specialized hydroponic equipment was designed by F. L. Wynd and is based on similar equipment originally designed by the Department of Agronomy, University of Illinois. The construction was carried out by the Service Department of Michigan State College. The pressure regulating device used in the hydroponic culture was designed by Charles A. Vana.

The frits: The glassy frits used in the investigation were designed by F. L. Wynd. The difficult technology of their manufacture was successfully accomplished by Charles A. Vana.

The analytical methods: The analytical methods were selected and organized to meet the routine requirements of the project by F. L. Wynd.

The greenhouse cultures: The first series of greenhouse cultures were carried out by R. L. LeBrec. The later series were carried out by E. R. Stromme.

The chemical analyses: The first analyses, comprising about one-third of the

I. INTRODUCTION

The results of many experiments have demonstrated the importance of minor elements in plant nutrition. Two of these elements, iron and manganese, have been studied with especial detail because they frequently limit crop production. Both of these nutrients are needed by plants in comparatively minute quantities and they usually are present in soils in amounts adequate for plant growth. The cause of deficiencies of these nutrients frequently depends on chemical and biological processes which render them unavailable to plants or which make them physiologically inactive within the plant.

A common example of a disturbance of the iron nutrition of plants is the so-called lime-induced chlorosis which is an important limiting factor in the production of certain tree fruits in several parts of the world. Bennett (1927) and Wallace (1929) demonstrated that this type of chlorosis could be eliminated by spraying the affected plants with dilute solutions of iron salts. Lime-induced chlorosis has been ascribed to the presence of excess calcium in the soil which leads to the precipitation of the iron.

However, it has been observed by Lindner and Harley (1944), Wallace (1928) and other workers that the concentration of iron in the dry matter of chlorotic leaves is not significantly different from that in comparable green leaves. Thorne and Wallace (1944), on the other hand, found significantly higher concentrations of iron in healthy leaves than in chlorotic leaves when the data were expressed on the basis of leaf area. The physiological disturbance causing chlorosis is far from being fully understood but it may be mentioned that Wallace and Hewitt (1946) believed that the immobility of iron, both in the external medium and within the plant, probably plays an important role in causing lime-induced chlorosis.

Although lime-induced chlorosis is a common cause of iron deficiency, other causes also are important under certain conditions. Olsen (1935) has demonstrated by growing plants in solution cultures that neutral or alkaline pH values affected the relationship between phosphate and iron, causing thereby an iron deficiency in the plant. Chandler and Scarseth (1941) found that the application of a phosphate salt to a slightly alkaline and to a highly calcareous clay produced iron chlorosis in peanuts. Similar results were reported by Sideris and Kraus (1933).

---

total, were carried out by R. L. LeBrec. The remaining two-thirds were carried out by Glenna Alylesworth and E. R. Stromme.

The present manuscript: E. R. Stromme presented a preliminary report on the entire project as a Doctorate Thesis. This preliminary report was revised and rewritten by F. L. Wynd for publication in Lloydia. The figures were drawn by M. Druckman.

The expenses of the project, including those of publication, were borne by the Ferro Corporation of Cleveland, Ohio.

[2]Graduate Research Fellow, Department of Botany and Plant Pathology, Michigan State College.

[3]Research Professor, Department of Botany and Plant Pathology, Michigan State College, East Lansing, Michigan.

McGeorge (1923), Johnson (1917), Rippel (1923), and Somers and Shive (1942) have shown that high concentrations of available manganese in soils or nutrient solutions induced chlorosis in plants and that this chlorosis could be avoided either by increasing the concentrations of iron in the nutrient solution or by spraying the plants with a dilute solution of an iron salt. The interrelationship between manganese and iron assumes a major importance in soils especially rich in manganese as are those in the Hawaiian Islands.

While iron deficiences may be caused by different factors, manganese deficiencies are due mainly to the oxidation and precipitation of manganese in the soil as reported by Connor (1932) and Willis (1932).

Schreiner and Dawson (1927), Skinner and Ruprecht (1930) and others have observed manganese deficiency in various crops grown on calcareous soils. Zimmerley (1926) and Gilbert, McLean, and Hardin (1926) observed this deficiency in crops grown on heavily limed soil.

An important instance of a manganese deficiency in crops is the gray speck disease of oats which is common in certain areas, The Australian investigators Samuel and Piper (1928), proved that the gray speck disease was caused by a deficiency of available manganese.

Manganese deficiency of oats has been reported by Willis (1928) and Alberts (1934) to occur on the eatern coastal plains of the United States and by Sherman and Harmer (1941) to occur in the alkaline organic solis of Michigan. It is now generally accepted by many investigators that manganese deficiency may occur when the soil is limed to a pH value greater than 6.5 and when the soil has strong oxidizing tendencies.[4]

The agricultural importance of deficiencies of iron and manganese in soils lies in the difficulty with which they are remedied. The addition of soluble salts of these nutrients or of sulphur to make the soil more acid, generally are of limited value because the conditions in the soil causing the original unavailability still exert their harmful effects.

Skinner and Ruprecht (1930) concluded from their experiments with truck crops grown on calcareous soil that much of the manganese added to the soil became unavailable within a period of three months. This situation caused Gilbert (1934) to conclude that it was necessary to apply manganese salts to alkaline soils before each crop was grown. Wallace and Ogelvie (1941) found that additions of manganese sulfate and manganese chloride were effective in combating manganese deficiency in Globe beets only during the early stages of their growth. Wain, Silk and Willis (1943) treated soils in the laboratory and in the laboratory and in the field with solutions of manganese sulfate and then examined at intervals the amount of manganese which could be extracted with neutral 1-normal ammonium acetate. They found in an experiment with a highly calcareous soil that the amount of extractable manganese fell to its original level after seven days.

In order to avoid the disturbing influence of soil factors, resort has been made to spraying plants or injecting them with iron and

[4]I do not concur with the current belief that the pH value itself is the important factor in causing chlorosis. The discussion of this controversial phenomenon lies beyond the scope of the present report.—F. L. WYND.

manganese salts. The latter procedure can be applied only to trees, and although effective in some instances, Wallace (1929) has shown that gumming of stone fruits may result. Sprays are sometimes unsatisfactory as they often are injurious at effective concentrations. In the case of lime-induced chlorsis, several sprayings must be made during a single season in order to supply the plants with a sufficient supply of iron.

In view of the difficulties encountered in maintaining a sufficient supply of available iron and manganese to plants growing under some conditions, the possibility of supplying these nutrients by adding artificially prepared physical complexes to the soil presents an intriguing approach to the problem. Such a material ideally should have the following properties: its aqueous solubility should be very low in order to prevent leaching and chemical reaction in the soil; the absorption of the ions by the plant root would have to take place necessarily by contact with the material; the material itself should be non-toxic to plants so that large amounts could be added to the soil to furnish the nutrients over a long period; the rate of release of the desired nutrient should be adequate for plant growth but should not attain a toxic magnitude.

The implication of contact absorption does not present a serious objection to the possibility of developing such a material. The active role of the root surfaces in absorbing nutrient ions from the solid phases of the soil already has been recognized. According to Jenny and Overstreet (1938), nutrients absorbed on the soil colloids are available to plant roots without the intervention of water-soluble phase. The process has been described as being an exchange of ions.

The ionic exchange mechanism proposed by Jenny and Overstreet will not necessarily explain a release to plant roots of nutrient ions held within a crystalline or amorphous matrix. However, there exists good evidence that plant roots have the ability to break down such structures to a limited extent and to obtain nutrients during the process. It has been reported that the highly insoluble mineral magnitite may serve as a source of iron for plants in hydroponic cultures. Eaton (1936) claimed that 0.1 percent of magnitite mixed with quartz sand made unnecessary the use of soluble iron in culture solutions if they were maintained on the acid side of neutrality. Some crop plants obtained sufficient amounts of iron from the magnitite even when the pH value was as high as 8.0. Chapman (1939) reported that Citrus seedlings grew satisfactorily in quartz gravel mixed with magnitite and flooded with a nutrient solution at pH values from 5.8 to 7.0. He found that the addition of calcium carbonate to the gravel caused chlorotic plants unless the amount of magnitite was correspondingly increased. This experiment suggested that there must be a sufficient area of contact between the magnitite and the plant roots in order to prevent chlorosis.

Guest (1944) used bentonite and magnitite mixed with quartz sand as a solid-phase source of certain nutrients in hydroponic cultures. Even at alkaline reactions of the nutrient solution, he found that chlorosis did not appear in citrus seedlings as long as the magnitite was finely ground in order to present a large surface area to the roots. The

addition of finely ground dolomite to the sand induced chlorosis which was assumed to be due to mechanical interference with the contact between the roots and the particles of magnitite.

Badger and Bray (1945) were the first to suggest the possibility of using especially compounded glass as a source of plant nutrients. These authors prepared glasses of such high solubility in water that they released significant amounts of nutritionally important ions. Studies were made on the effect of the melting temperature on the solubility of the glass made of rock phosphate, potash and silica, and it was found that glasses could be prepared which were surprisingly soluble with respect to phosphorus and potassium. The work was not extended to include other elements nor were any nutritional experiments carried out. There is reason to believe that their materials would have imparted high pH values to the medium, but no pH measurements were reported.

The present study was carried out in order to further investigate the materials which were shown by Wynd (1950, 1951) and his coworkers to retain iron and manganese in a relatively insoluble form would release these nutrients by contact with the absorbing root surfaces. The frits were amorphous in structure and their physical and chemical properties were varied between wide limits by changing their chemical compositions and the procedures of their manufacture. The present investigation was directed especially towards determining the influence of the pH value of the medium on the release of iron and manganese to the experiment plants grown in hydroponic cultures.

II. Experimental Methods and Materials

A. Methods

The effects of the pH values of the nutrient solution on the availabilities of iron and manganese in the experimental frits were studied by growing wheat in hydroponic pot cultures using the frit in place of the usual gravel. A quartz culture served as a control for each individual frit culture by being flooded repeatedly with identical nutrient solution in the manner described by Wynd (1951). This quartz culture was designated as the "corresponding control" as it was associated with a single frit culture. The differences between the growth and chemical composition of the plants grown in the frit and in its corresponding control culture were taken as indications of the relative importance of contact absorption and absorption dependent on the aqueous solubility of the iron and manganese in the frit.

Any soluble material released from the frit would become equally distributed between its culture and its corresponding control culture. If the experimental frit should release soluble nutrients, both cultures would profit equally. On the other hand, if the plants growing in the frit were able to obtain nutrients by contact absorption, they would be expected to be superior to those growing in the corresponding control culture. All frits were studied in duplicate, and each frit culture was coupled with its individual corresponding quartz control.

Since the purpose of the study was to determime the availability of iron and manganese in frits, as influenced by the pH value of the solutions, two types of frits were used. One contained iron but no

manganese, and the other contained both iron and manganese. The nutrient solutions which periodically flooded the pots containing the iron-bearing frit and its corresponding control pot were complete except that no iron was added. The solutions which flooded the frits containing both iron and manganese were complete except that neither of these nutrients was added.

A three-salt solution similar to that described by Shive (1915) was used as the nutrient medium. The solutions also contained the following concentrations of trace nutrients expressed as parts per million: boron, 0.50; zinc, 0.05; molybdenum, 0.05; copper, 0.02. When the frits contained no manganese, the nutrient solutions also contained 0.5 parts per million of manganese.

Absolute control cultures using quartz gravel were arranged as described above. Iron and manganese were added to these nutrient solutions as indicated below:

Absolute control culture	Fe p.p.m.	Mn p.p.m.
1	4.0	0.5
2	0	0.5
3	4.0	0
4	0	0

The acidity of the nutrient solution was expected to influence the rate at which the iron and manganese in the frits would be released to the plant roots or brought into solution. A constant predetermined pH value was therefore maintained. The pH value of the solution in each individual carboy was determined twice a week with a glass electrode and adjusted when necessary to the predetermined value by the addition of 1-normal sulphuric acid or 1-normal potassium hydroxide. The pH values were maintained within 0.2 pH unit of the value predetermined by the plan of each experiment.

Forty-five seeds of wheat of the variety Illinois, harvested in 1948, were planted one inch deep in the experimental frits and their control cultures, From 30 to 40 plants were grown in each pot. No effort was made to obtain a uniform number of plants per pot since the removal of plants severely disturbed the root systems of those remaining. The plants were harvested at the jointing stage. The growth period of each experiment was about 45 days.

The roots were separated from the tops and discarded when the plants were removed from the culture pots for study. The lower part of the stems, which had been in contact with the nutrient solution, was washed in runnung tap water, rinsed in distilled water, and gently wiped with cheesecloth. The material was dried in forced-air chamber at a temperature of 60° C.

The dry material was finely ground and one-gram samples were weighed into platium crucibles and ignited at 850° C. for two hours. After cooling, the ash was moistened with one milliliter of a 1:4 sulphuric acid solution, and about five milliliters of concentrated hydrofluoric acid were added. The crucible was then placed on an electric hot plate at low heat, and the solution was evaporated until only a viscous residue

remained. About ten milliliters of a 0.1-normal nitric acid solution were added while the crucible was on the hot plate. The dissolved residue was transferred to a 50-milliliter volumetric flask, cooled. and brought to volume with 0.1-normal nitric acid.

Iron was determined in the solution by the colorimetric procedure using o-phenanthroline as described by Hummell and Willard (1938). Manganese was determined colorimetrically by the periodate method described by Willard and Greathouse (1917).

Samples of the nutrient solutions were collected at the end of the growing periods. In order to obtain a representative sample, five milliliters of concentrated sulphuric acid were added to each carboy. The acidified solution was well shaken and the sample collected while the carboy was being emptied. The solution was filtered, and 500 milliliters were transferred to a 600-milliliter beaker and evaporated on a hot plate to a volume of about 50 milliliters. The concentrated solution was transferred to a 100-milliliter flask. After cooling, the solution was brought to volume with distilled water. Iron and manganese in the concentrated sample of the nutrient solution were determined by the methods cited above.

The amounts of potassium and sodium released to the nutrient solution by each frit were determined by the Perkin-Elmer flame photometer, Model No. 52C, using an acetylene flame. A 2-milliliter aliquot of the concentrated nutrient solution was pipetted into a 50-milliliter volumetric flask and brought to volume with distilled water.

B. FRITS

Technical grades of raw materials were used in compounding the experimental frits, such as powdered quartz, potassium carbonate, sodium carbonate, mono-calcium phosphate, etc. The well mixed components were melted in an electric smelter and held in the molten stage for 3.5 hours. The molten material was quenched by permitting it to flow into cold running water. The material was fragmented into small pieces by the rapid cooling in the water. The moist, fragmented material was cooled and dried in a commercial rotary drying pan, and then the particles were graded for size by a series of screens. The material selected for the experiments was about one-eight of an inch in diameter.

Before the frits were placed in the culture pots, they were passed through a 2-millimeter sieve to remove the finer particles. The material retained on the sieve was washed in tap water and rinsed with distilled water.

Quartz gravel was sieved as described for the frit in order to obtain particles equalling the frits in size and uniformity. The quartz gravel was spread in a thin layer and exposed to a strong electro-magnet to remove particles of iron introduced by grinding machinery. It was then leached for several days with dilute sulphuric acid thoroughly washed with tap water, and rinsed with distilled water.

The compositions of the frits used in the present study were based upon results obtained by Wynd (1950, 1951) and his co-workers in previous studies of iron-containing frits. This earlier work may be summarized as follows: The compositions of the frits were based

arbitrarily on the data presented by Badger and Bray (1945). The frits obtained varied greatly in their aqueous solubilities. The solubilities of the frits were found to exert a marked influence on the growth of the plants. A solubility above 7.0 percent rendered the nutrient solutions so alkaline that they were toxic to the experimental plants. The most successful cultures produced wheat plants which compared favorably in growth with those produced by the absolute control cultures receiving a complete nutrient solution. The best frits were those exhibiting a relatively low solubility. Chlorosis did appear, however, in the later stages of the growing period, and in subsequent experiments the Fe_2O_3 content of the frits was increased from 2.0 to 5.0 percent.

Some of the latter frits containing 5 percent Fe_2O_3 produced plants which were green and healthy throughout the experimental period and which were superior in size to those grown in the absolute control cultures receiving a complete nutrient solution. The compositions and the solubilities of the newer frits are listed in table 1. The table

TABLE 1. *Chemical composition of frits and their solubilities, expressed as percentages, used in preliminary studies on the availability of iron in frit to wheat plants.*

Group	Frit No.	Fe_2O_3	SiO_2	P_2O_5	CaO	MgO	K_2O	Na_2O	Solubility
1	6224-A	5.0	66.0	5.0	5.6	3.6	7.4	7.4	0.8
	6224-B	5.0	62.4	10.0	5.3	3.5	6.9	6.9	0.6
	6224-C	5.0	58.6	15.0	5.0	3.3	6.6	6.6	0.3
2	6238-A	5.0	46.0	8.4	9.4	6.1	12.5	12.5	20.0
	6238-B	5.0	43.7	15.8	8.4	5.5	10.9	10.9	8.0
	6238-C	5.0	40.4	21.8	8.6	4.8	9.6	9.6	2.0
3	6241-A	5.0	36.4	10.1	11.3	7.2	15.0	15.0	36.0
	6241-B	5.0	34.3	18.6	9.9	6.5	12.9	12.9	31.0
	6241-C	5.0	31.7	25.3	10.0	5.6	11.2	11.2	11.0

includes three groups of frits representing three different levels of silica content. Within each group a decrease in the percentage of CaO, MgO, K_2O, Na_2O with a corresponding increase in the phosphorus content resulted in decreased solubility.

Of the frits listed in table 1. 6238-C and 6224-C produced the best plants as judge by the fresh weight obtained. Frits of the 6238-C series produced slightly greater fresh weights of plants than frits of the 6224-C series. On the basis of the total amount of iron absorbed per plant, 6224-C gave higher values than 6238-C. The basic formulae represented by these two frits therefore were selected for the present study. Since both had proved successful, the investigations had reached the point where it was appropriate to explore the effects of changes in their iron content. At this stage manganese also was included in the study, and the four series of frits listed in table 2 were prepared by Charles A. Vana, of the Ferro Corporation.

The frits of the 6285 and 6287 series in table 2 conform to the basic formula represented by 6238-C and the 6286 and 6288 series conform to the basic formula represented by 6224-C in table 1. The variation

in iron and manganese in the new frits, as shown in table 2, were compensated by a proportional change in the other constituents to avoid appreciable deviations from the basic formula.

TABLE 2. *Chemical composition, expressed as percentages, of frits used in the present study on the availability of iron and manganese in frit to wheat plants.*

Frit	Fe_2O_3	MnO_2	CaO	MgO	K_2O	Na_2O	P_2O_5	SiO_2
6285-A	2.5	0	8.9	5.0	9.85	9.85	22.2	41.6
6285-B	5.0	0	8.6	4.8	9.6	9.6	21.8	40.4
6285-C	7.5	0	8.4	4.7	9.34	9.34	21.2	39.4
6285-D	10.0	0	8.2	4.6	9.1	9.1	20.5	38.3
6287-A	5.0	1.0	8.5	4.7	9.5	9.5	21.6	40.0
6287-B	5.0	2.0	8.5	4.7	9.4	9.4	21.4	39.6
6287-C	5.0	3.0	8.3	4.6	9.3	9.3	21.2	39.2
6287-D	5.0	4.0	8.2	4.6	9.2	9.2	20.9	38.8
6286-E	2.5	0	6.0	3.4	6.9	6.9	15.4	59.3
6286-F	5.0	0	5.9	3.3	6.7	6.7	15.0	57.7
6286-G	7.5	0	5.7	3.2	6.6	6.6	14.6	56.2
6286-H	10.0	0	5.6	3.1	6.4	6.4	14.2	54.7
6288-E	5.0	1.0	5.8	3.2	6.6	6.6	14.8	57.3
6288-F	5.0	2.0	5.8	3.2	6.6	6.6	14.7	56.8
6288-G	5.0	3.0	5.7	3.2	6.5	6.5	14.5	56.0
6288-H	5.0	4.0	5.6	3.2	6.4	6.4	14.4	55.6

All frits were studied simultaneously at various pH levels of the nutrient solution. The following experiments were carried out:

Experiment No.	pH of nutrient solution	Growth period by dates	Growth Period in days
1	6.0	June 13 to July 26.....	43
2	7.0	September 10 to October 24.....	44
3	4.0	November 7 to December 22.....	45
4	5.0	December 28 to February 14.....	48

III. EXPERIMENTAL RESULTS

A. VISUAL CHARACTERISTICS OF THE PLANTS

Nutrient solution maintained at pH = 4.0: The experiment with nutrient solutions maintained at pH = 4.0 was carried out during the months of November and December and the plants grew relatively slowly because of the low light intensity. In spite of the low growth, pronounced differences in the size of the plants and in the color of their leaves were observed between the plants grown in the frits and their corresponding control cultures. In all instances, the size of the plants grown in the frit cultures was larger than that attained by the plants grown in their corresponding control cultures. In most instances, the plants grown in the frits were darker green in color than those grown in their corresponding control cultures.

It was noticeable also that the plants grown in the frits of the 6285 and 6287 series which contained the lower percentages of silica were larger than those grown on frits of the 6286 and 6288 series. Similar differences were observed between the plants grown in the corresponding control cultures, the largest plants being associated with the largest frit-grown plants.

No visible differences were apparent between the plants grown on each individual series of frits. This indicated that the different percentages of iron and manganese in the frits exerted no visible effect on the plants.

The color of the *absolute* control plants grown without iron was less green than those supplied with a complete nutrient solution. No deficiency symptoms were observed in the absolute control cultures from which manganese was excluded. The size of the iron-deficient absolute control plants was not appreciably smaller than the size of those which received a complete nutrient solution. However, these absolute control plants were smaller than those grown in the frits of the 6285 and 6287 series.

Nutrient solution maintained at pH = 5.0: The experiment with the nutrient solutions maintained at pH = 5.0 was carried out during the months of January and February. The installation of adequate electric lights materially improved the growth of the plants.

All of the frit-grown plants were green and healthly at the end of the experimental period. On the other hand, all of their corresponding control plants exhibited chlorosis early in the experimental period and their growth was markedly inhibited.

Again it was observed that the frits of the 6285 and 6287 series produced larger plants than did those of the 6286 and 6288 series, and a similar difference again was noticeable between the corresponding control plants. The corresponding control plants for the 6285 and 6287 series of frits also were larger than the corresponding control plants produced by the 6286 and 6288 series of frits. At the time of harvest, the plants grown in frit had started to joint, while very very few of their corresponding control plants had reached this stage of development.

Within each frit series, the plants did not exhibit any visible differences which could be correlated with the different percentages of iron or manganese in the frits. However in case of the series 6287, the frit containing 2 percent manganese dioxide produced definitely taller plants than did the other frits of this series. The corresponding control cultures of this frit likewise produced definitely taller plants than did the other control cultures of the series.

The *absolute* control cultures receiving no iron in the nutrient solution produced very chlorotic plants and their growth was greatly inhibited. The omission of manganese from the nutrient solution resulted in a slight chlorosis of the plants, although their growth did not appear to have been visibly affected by their chlorotic condition. The complete nutrient solution produced normal and healthy plants, but in no instances did their growth equal that of the plants grown in the frits of the 6285 and 6287 series.

Nutrient solution maintained at pH = 6.0: The experiment with

the nutrient solutions maintained at pH = 6.0 was carried out during the months of June and July. It was difficult to avoid high temperatures in the greenhouse on bright days and drying of the leaf tips occurred in some instances.

In general, the same visible results were obtained as described for the previous experiment. The corresponding control plants became chlorotic at an early stage of their development and their size was markedly less than that of the plants grown in the frit cultures.

The plants grown on frit 6287-B containing 2.0 percent manganese dioxide reached an exceptionally large size. The frits of the 6285 and 6287 series produced larger plants than did the absolute control cultures receiving complete nutrient solution. The growth of the absolute control plants receiving iron was inferior to the growth of the best frit-borne plants.

Manganese deficiency did not occur in this nor in the following experiment when it was excluded from nutrient solution of the absolute control cultures. Iron deficiency, on the other hand, became very prominent in the cultures lacking iron.

Nutrient solution maintained at pH = 7.0: The experiment with the nutrient solution maintained at pH = 7.0 was carried out during the months of September and October. The plants grew slowly, partly because of the low light intensity and partly because of the unfavorable pH value.

The differences in growth between the plants grown in the frit cultures and in their corresponding control cultures were more pronounced at this pH value than pH values of 4.0, 5.0, or 6.0. The corresponding control plants attained only about half the size of the frit-borne plants. The corresponding control plants were very chlorotic in all instances. It was again conspicuously evident that the plants grown in the frits of the 6285 and 6287 series were superior to those grown in the frits of the 6286 and 6288 series.

The development of the plants in the *absolute* control cultures was similar to that described for the experiment with the nutrient solutions maintained at pH = 6.0.

Summary of the visible appearances of the plants: The visual observations of the development of the plants grown at the different pH values can be summarized as follows:

1. The frit cultures produced normal, green plants over a range of pH values of the nutrient solutions from 4.0 to 7.0.
2. The *corresponding* control cultures for the frits produced more or less chlorotic plants, and their growth was inferior to that of the frit-borne plants. The degree of chlorosis and the difference in growth between the corresponding control plants and the frit grown plants increased as the pH value of the nutrient solution was increased.
3. At all pH values of the nutrient solution frits of the 6285 and and 6287 series produced plants conspicuously larger than the absolute control plants which received complete nutrient solutions.
4. The growth of the plants in the corresponding control cultures seemed to be related to the growth of the plants in the frit cultures, as a good growth of the frit-borne plants was associated with a good growth of their corresponding control plants.

TABLE 3. *Fresh weight, expressed as grams per ten plants, produced by the frits and their corresponding quartz control cultures supplied with nutrient solution at pH = 4.0.*

FRIT			FRESH WEIGHT PER 10 PLANTS							
No.	Composition (percent)		Culture 1		Culture 2		Average		Percentage of the absolute control plants receiving Fe and Mn	
	Fe_2O_3	MnO_2	Quartz	Frit	Quartz	Frit	Quartz	Frit	Quartz	Frit
6285-A	2.5	0	10.5	13.9	10.4	14.3	10.5	14.1	115	155
6285-B	5.0	0	9.9	10.7	11.2	13.6	10.6	12.2	116	134
6285-C	7.5	0	11.5	15.0	9.4	12.3	10.5	13.7	115	151
6285-D	10.0	0	8.9	14.6	9.5	13.1	9.2	13.9	101	153
6287-A	5.0	1.0	12.6	13.2	11.8	12.9	12.2	13.1	134	144
6287-B	5.0	2.0	10.5	13.9	10.4	13.6	10.5	13.7	115	151
6287-C	5.0	3.0	10.4	14.6	9.7	12.7	10.1	13.7	111	151
6287-D	5.0	4.0	10.8	13.3	10.4	12.1	10.6	12.7	116	140
6286-E	2.5	0	8.5	11.4	8.2	12.1	8.4	11.8	92	130
6286-F	5.0	0	8.5	10.5	7.6	13.4	8.1	12.0	89	132
6286-G	7.5	0	8.6	10.4	9.4	10.6	9.0	10.5	99	115
6286-H	10.0	0	7.4	9.9	11.9	12.3	9.7	11.1	107	122
6288-E	5.0	1.0	9.2	9.9	10.4	11.7	9.8	10.8	108	119
6288-F	5.0	2.0	9.3	11.4	6.1	9.8	7.7	10.6	85	116
6288-G	5.0	3.0	8.8	9.3	8.4	11.3	8.6	10.3	95	113
6288-H	5.0	4.0	9.1	11.1	8.9	10.9	9.0	11.0	99	121

5. The visible appearances of the frit-grown plants clearly showed the increasingly favorable effect of the frits, as compared with the the corresponding culture plants, as the pH values of the nutrient solutions were increased.

B. FRESH WEIGHT OF THE PLANTS

The fresh weights of the plants obtained from the individual cultures maintained at the various pH values are presented in tables 3 to 10 inclusive.

The data show that the fresh weights of the plants obtained from the individual frit cultures at all pH levels were significantly greater than the weights obtained from their corresponding control cultures. Also the fresh weights of the corresponding control plants were closely related to the fresh weights of the plants grown in the frits. That is to say, a relatively large fresh weight of the frit-borne plants generally was associated with a relatively large fresh weight of their corresponding control plants.

TABLE 4. *Fresh weight, expressed as grams per ten plants, produced by the absolute control cultures supplied with nutrient solution of pH = 4.0*

TREATMENT		CULTURE 1		CULTURE 2		CULTURE 3		AVERAGE	RELATIVE AVERAGE
Fe p.p.m.	Mn p.p.m.	Pot 1	Pot 2	Pot 1	Pot 2	Pot 1	Pot 2		
4.0	0.5	6.6	6.7	10.3	13.3	8.4	9.2	9.1	100
0	0.5	7.1	7.6	10.5	10.5	11.3	11.3	9.7	107
4.0	0	8.6	8.0	9.1	8.2	8.3	8.3	8.4	92
0	0	3.1	3.3	9.4	9.1	9.4	9.9	7.3	80

The frits of the 6285 and the 6286 series invariably produced larger yields of fresh plant material than the frits of the 6286 and 6288 series, and similarly the fresh weights obtained from the corresponding control cultures of the 6285 and 6287 frit series were larger than obtained from the corresponding control cultures of the frits of the 6286 and 6288 series.

The average fresh weights obtained from the individual cultures, calculated as percentages of the average fresh weights obtained from the *absolute* control culture receiving complete nutrient solution, are presented in relation to the frit compositions in figures 2 to 5 inclusive. These figures show that at all pH values of the nutrient solution, the fresh weights produced by the 6285 and 6287 frit cultures were significantly greater than those obtained from the *absolute* control cultures receiving a complete nutrient solution. The same is true for the fresh weights obtained from the 6286 and 6288 frit cultures excepting when the nutrient solution was maintained at pH = 5.0. In this latter case, the plants grown in these frits attained about the the same fresh weight as the absolute control plants receiving the complete nutrient solution.

TABLE 5. *Fresh weight, expressed as grams per ten plants, produced by the fritz and their corresponding quartz control cultures supplied with nutrient solution of pH = 5.0.*

FRIT			FRESH WEIGHT PER 10 PLANTS							
No.	Composition (percent)		Culture 1		Culture 2		Average		Percentage of the absolute control plants receiving Fe and Mn	
	Fe_2O_3	MnO_2	Quartz	Frit	Quartz	Frit	Quartz	Frit	Quartz	Frit
6285-A	2.5	0	11.3	26.8	19.1	26.4	15.2	26.6	70	123
6285-B	5.0	0	17.0	22.1	22.1	27.5	19.6	24.8	90	114
6285-C	7.5	0	18.5	22.8	17.5	26.3	18.0	24.6	83	113
6285-D	10.0	0	23.2	27.0	21.2	26.7	22.2	26.9	102	124
6287-A	5.0	1.0	23.7	21.0	12.5	26.4	18.1	23.7	83	109
6287-B	5.0	2.0	23.5	31.0	27.8	30.9	25.7	31.0	118	143
6287-C	5.0	3.0	21.2	32.2	20.9	25.8	21.1	29.0	97	134
6287-D	5.0	4.0	19.3	27.5	17.7	28.5	18.5	28.0	85	129
6286-E	2.5	0	20.3	20.9	13.6	20.9	17.0	20.9	78	96
6286-F	5.0	0	17.6	20.6	15.4	23.4	16.5	22.0	76	101
6286-G	7.5	0	13.2	19.4	16.8	21.5	15.0	20.5	69	94
6286-H	10.0	0	16.7	21.3	17.5	24.7	17.1	23.0	79	106
6288-E	5.0	1.0	14.2	19.3	7.2	22.4	10.7	20.9	49	96
6288-F	5.0	2.0	12.9	20.8	4.2	17.6	8.6	19.4	40	89
6288-G	5.0	3.0	12.1	14.1	8.8	21.6	10.5	17.9	48	82
6288-H	5.0	4.0	13.1	18.5	4.6	23.0	8.9	20.8	41	96

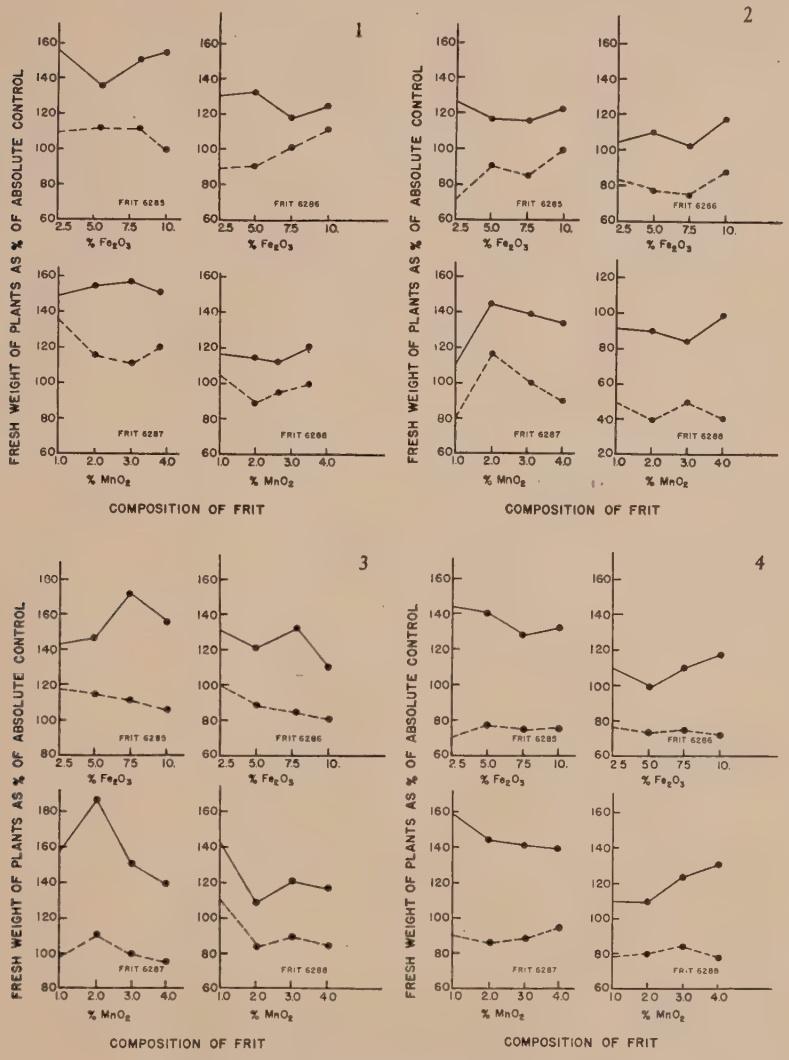

FIG. 1. Average fresh weights of plants grown in frits and their corresponding control cultures, expressed as percentages of the absolute control values. Nutrient solutions pH = 4.0.

FIG. 2. Average fresh weights of plants grown in frits and their corresponding control cultures, espressed as percentages of the absolute control values. Nutrient solutions pH = 5.0.

FIG. 3. Average fresh weights of plants grown in frits and their corresponding control cultures, expressed as percentages of the absolute control values. Nutrient solutions pH = 6.0.

FIG. 4. Average fresh weights of plants grown in frits and their corresponding control cultures, expressed as percentages of the absolute control values. Nutrient solutions pH = 7.0.

In all figures: frits, solid lines; corresponding controls, broken lines.

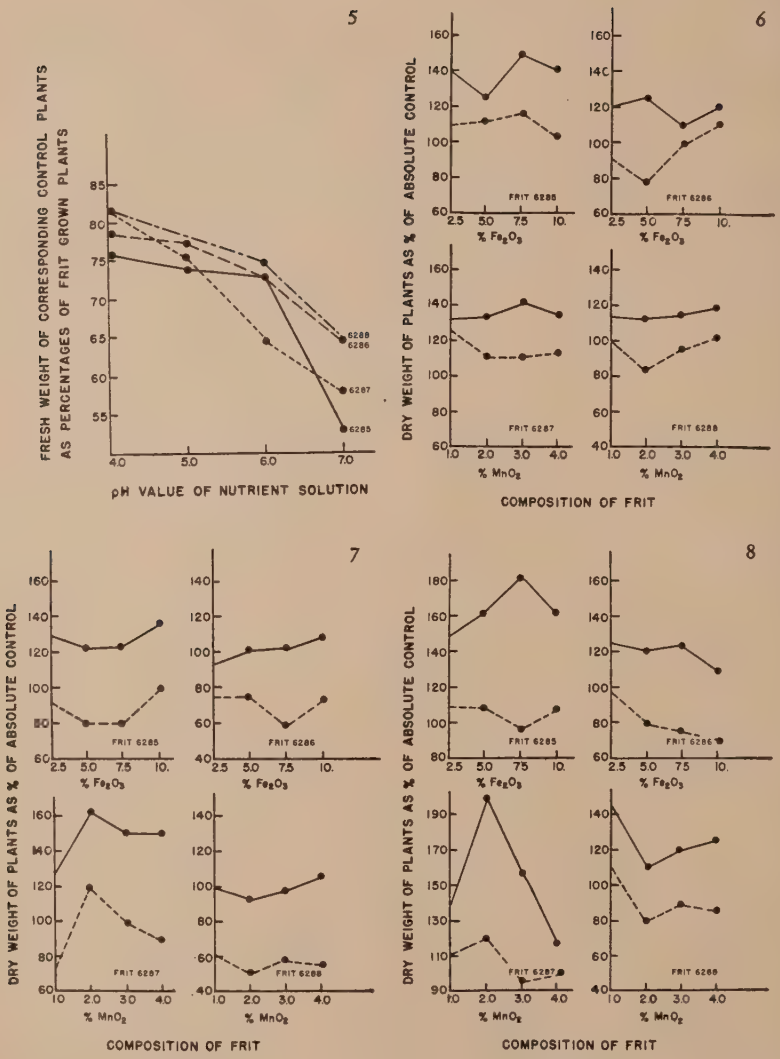

FIG. 5. Average fresh weights of the corresponding control plants, expressed as percentages of the frit-grown plants, as influenced by the pH values of the nutrient solutions.

FIG. 6. Average dry weights of plants grown in frits and their corresponding control cultures, expressed as percentages of the absolute control values. Nutrient solutions pH = 4.0.

FIG. 7. Average dry weights of plants grown in frits and their corresponding control cultures, expressed as percentages of the absolute control values. Nutrient solutions pH = 5.0.

FIG. 8. Average dry weights of plants grown in frits and their corresponding control cultures, expressed as percentages of the absolute control values. Nutrient solution pH = 6.0.

The figures also show that within each individual frit series there were differences in the fresh weights of the plants and that these differences paralleled changes in the weights of the plants from their corresponding control cultures. The figures show that the fresh weights of the plants were not correlated with the amount of iron or manganese in the frits. At pH values of 5.0 to 6.0 (figures 3 and 4), frit 6287-B containing 2.0 percent manganese dioxide produced an exceptionally large fresh weight of plants which indicated that this frit represented the most favorable composition within the series with respect to the percentage of iron and manganese.

TABLE 6. *Fresh weight, expressed as grams per ten plants, produced by the absolute control cultures supplied with nutrient solution of pH = 5.0.*

TREATMENT		CULTURE 1		CULTURE 2		CULTURE 3		AVERAGE	RELATIVE AVERAGE
Fe p.p.m.	Mn p.p.m.	Pot 1	Pot 2	Pot 1	Pot 2	Pot 1	Pot 2		
4.0	0.5	23.2	18.2	23.6	25.1	20.3	19.6	21.7	100
0	0.5	12.6	13.5	12.0	14.4	13.8	15.2	13.6	63
4.0	0	17.0	16.4	16.6	14.7	21.9	22.0	18.1	83
0	0	12.0	12.2	10.5	9.0	16.8	16.3	12.8	59

TABLE 7. [*See p. 18.*]

TABLE 8. *Fresh weight, expressed as grams per ten plants, produced by the absolute control cultures supplied with nutrient solution of pH = 6.0.*

TREATMENT		CULTURE 1		CULTURE 2		CULTURE 3		AVERAGE	RELATIVE AVERAGE
Fe p.p.m.	Mn p.p.m.	Pot 1	Pot 2	Pot 1	Pot 2	Pot 1	Pot 2		
4.0	0.5	21.9	22.0	22.6	24.9	24.5	26.3	23.7	100
0	0.5	23.5	22.1	16.0	17.9	25.5	26.8	22.0	93
4.0	0	21.6	22.1	22.2	22.4	.....	.....	22.1	93
0	0	16.4	19.5	22.9	21.5	14.1	16.3	18.5	78

The average fresh weights obtained from the corresponding control cultures within each individual series of frits were calculated as percentages of the average fresh weights obtained from the frit cultures. The values obtained were plotted against the pH value of the nutrient solution in figure 6. The effect of raising the pH value from 4.0 to 7.0 was to increase the differences between the frit grown plants and their corresponding control plants. The exceptionally low percentage obtained at pH = 5.0, especially in the case of the 6288 frit series, might have been due to the differences in the physiological ages of the frit-borne plants and the corresponding control plants in this experi-

TABLE 7. *Fresh weight, expressed as grams per ten plants, produced by the frits and their corresponding quartz control cultures supplied with nutrient solution of pH = 6.0.*

FRIT			FRESH WEIGHT PER 10 PLANTS							
No.	Composition (percent)		Culture 1		Culture 2		Average		Percentage of the absolute control plants receiving Fe and Mn	
	Fe_2O_3	MnO_2	Quartz	Frit	Quartz	Frit	Quartz	Frit	Quartz	Frit
6285-A	2.5	0	29.4	33.8	24.1	35.6	26.8	34.7	113	146
6285-B	5.0	0	29.1	39.5	24.7	33.9	26.9	36.7	114	155
6285-C	7.5	0	28.2	43.3	24.6	37.1	26.4	40.2	111	170
6285-D	10.0	0	23.8	33.8	25.9	36.0	24.9	34.9	105	147
6287-A	5.0	1.0	20.9	28.5	24.5	41.8	22.7	35.2	96	149
6287-B	5.0	2.0	22.2	39.3	27.6	46.7	24.9	43.0	105	181
6287-C	5.0	3.0	23.3	33.8	22.6	33.2	23.0	33.5	97	141
6287-D	5.0	4.0	21.1	32.3	19.5	27.7	20.3	30.0	86	127
6286-E	2.5	0	19.9	27.0	26.8	32.5	23.4	29.8	99	126
6286-F	5.0	0	14.7	26.2	24.9	28.9	19.8	27.6	84	116
6286-G	7.5	0	15.0	27.3	22.3	29.9	18.7	28.6	79	121
6286-H	10.0	0	11.5	19.6	22.6	26.9	17.1	23.3	72	98
6288-E	5.0	1.0	23.0	31.7	28.1	35.9	25.6	33.8	108	143
6288-F	5.0	2.0	20.4	25.1	.....	.....	20.4	25.1	86	106
6288-G	5.0	3.0	21.6	27.5	20.6	28.8	21.1	28.2	89	119
6288-H	5.0	4.0	19.5	22.4	20.0	32.3	19.8	27.4	84	116

TABLE 9. *Fresh weight, expressed as grams per ten plants, produced by the frits and their corresponding quartz control cultures supplied with nutrient solution of pH = 7.0.*

FRIT			FRESH WEIGHT PER 10 PLANTS							
No.	Composition (percent)		Culture 1		Culture 2		Average		Percentage of the absolute control plants receiving Fe and Mn	
	Fe_2O_3	MnO_2	Quartz	Frit	Quartz	Frit	Quartz	Frit	Quartz	Frit
6285-A	2.5	0	5.3	10.9	5.8	11.4	5.6	11.2	72	144
6285-B	5.0	0	6.8	11.1	5.0	10.6	5.9	10.9	76	140
6285-C	7.5	0	6.3	10.4	4.7	9.4	5.5	9.9	71	127
6285-D	10.0	0	5.4	10.0	6.2	10.6	5.8	10.3	74	132
6287-A	5.0	1.0	7.2	11.5	6.0	13.3	6.6	12.4	85	159
6287-B	5.0	2.0	6.5	10.9	6.5	11.3	6.5	11.1	83	142
6287-C	5.0	3.0	6.6	10.4	6.4	11.2	6.5	10.8	83	138
6287-D	5.0	4.0	5.8	10.1	7.4	10.4	6.6	10.3	85	132
6286-E	2.5	0	5.6	8.1	5.7	9.0	5.7	8.6	73	110
6286-F	5.0	0	5.1	7.0	5.9	8.3	5.5	7.7	71	99
6286-G	7.5	0	5.5	8.5	5.0	8.4	5.3	8.5	68	109
6286-H	10.0	0	5.1	8.4	5.7	9.4	5.4	8.9	69	114
6288-E	5.0	1.0	5.1	7.9	6.5	9.5	5.8	8.7	74	112
6288-F	5.0	2.0	6.4	7.5	5.8	9.7	6.1	8.6	78	110
6288-G	5.0	3.0	5.8	8.1	6.8	10.6	6.3	9.4	81	121
6288-H	5.0	4.0	5.0	9.0	5.9	10.7	5.5	9.9	71	127

ment. At the time of harvest, the frit-borne plants had begun to joint, while the corresponding control plants had not reached this stage In the other experiments the plants were harvested at a somewhat earlier stage of their development.

TABLE 10. *Fresh weight, expressed as grams per ten plants, produced by the absolute control cultures supplied with nutrient solution of pH = 7.0.*

TREATMENT		CULTURE 1		CULTURE 2		CULTURE 3		AVERAGE	RELATIVE AVERAGE
Fe p.p.m.	Mn p.p.m.	Pot 1	Pot 2	Pot 1	Pot 2	Pot 1	Pot 2		
4.0	0.5	6.5	6.6	8.5	7.9	8.1	9.4	7.8	100
0	0.5	7.0	6.7	5.1	4.5	7.5	7.3	6.4	82
4.0	0	9.3	9.1	7.6	6.8	10.4	11.0	9.0	115
0	0	5.8	6.0	5.5	5.6	7.9	8.3	6.5	83

C. DRY WEIGHT OF PLANTS

The dry weights of the plants obtained from the individual cultures maintained at the different pH values are listed in tables 11 to 18 inclusive.

The data show that at all pH values the dry weights of the plants obtained from the frit cultures were significantly larger than those obtained from their corresponding control cultures. The data also show that the dry weights of the corresponding control plants were correlated with the dry weights of the plants grown in the frit cultures.

It was further evident from figures 7 to 10 inclusive that the frit series 6285 and 6287, at all pH levels, produced significantly higher yields of dry plant material than did the the *absolute* control culture receiving the complete nutrient solution. The same result was obtained with frits of the 6286 and 6288 series excepting when the pH value of the nutrient solution was 5.0. At this pH value, the dry weights of the plants grown in these frits were not significantly different from the weights obtained from the absolute control cultures receiving the complete nutrient solution.

The figures do not indicate any correlation between the amount of iron or manganese present in the frit and the dry weight of the plants produced. It is evident, however, that frit 6287-B containing 2.0 percent manganese dioxide increased the dry weight of the plants about 100 percent as compared to the weight obtained from the absolute control cultures receiving the complete nutrient solution, and it also is evident that the frit 6285-C containing 7.5 percent ferric oxide increased the dry weight about 80 percent when the data were calculated in the same manner.

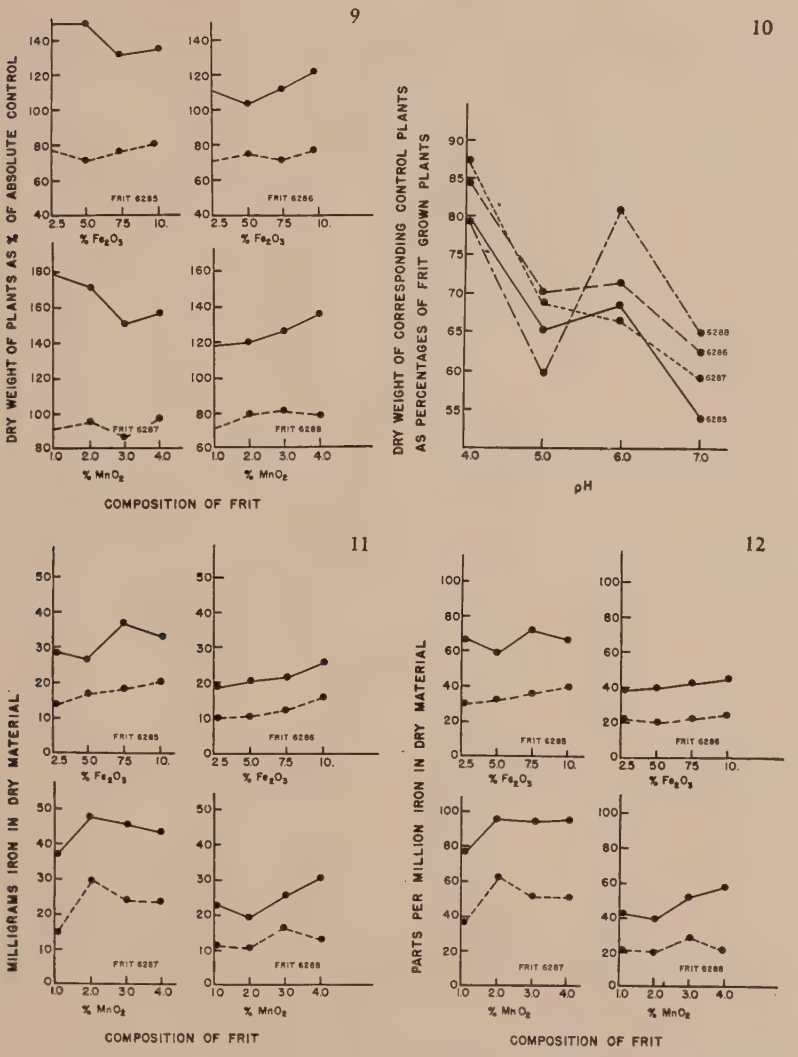

FIG. 9. Average dry weights of plants grown in frits and their corresponding control cultures, expressed as percentages of the absolute control values. Nutrient solutions pH = 7.0.

FIG. 10. Average dry weights of the corresponding control plants, expressed as percentages of the frit-grown plants, as influenced by the pH value of the nutrient solution.

FIG. 11. Milligrams of iron in the dry material of plants grown in frits and their corresponding control cultures. Nutrient solutions of pH = 5.0.

FIG. 12. Parts per million of iron in the dry material of plants grown in frits and their corresponding control cultures. Nutrient solutions pH = 5.0.

TABLE 11. *Dry weight, expressed as grams per ten plants, obtained from the frits and their corresponding control cultures supplied with nutrient solution of pH = 4.0.*

FRIT			DRY WEIGHT PER 10 PLANTS							
No.	Composition (percent)		Culture 1		Culture 2		Average		Percentage of the absolute control plants receiving Fe and Mn	
	Fe_2O_3	MnO_2	Quartz	Frit	Quartz	Frit	Quartz	Frit	Quartz	Frit
6285-A	2.5	0	1.33	1.73	1.35	1.74	1.34	1.74	108	140
6285-B	5.0	0	1.30	1.38	1.44	1.64	1.37	1.51	110	122
6285-C	7.5	0	1.59	2.00	1.15	1.54	1.37	1.77	110	143
6285-D	10.0	0	1.19	1.76	1.23	1.60	1.21	1.68	98	135
6287-A	5.0	1.0	1.63	1.67	1.53	1.61	1.58	1.64	127	132
6287-B	5.0	2.0	1.38	1.79	1.37	1.46	1.38	1.63	111	131
6287-C	5.0	3.0	1.41	1.82	1.30	1.66	1.36	1.74	110	140
6287-D	5.0	4.0	1.44	1.66	1.36	1.55	1.40	1.61	113	130
6286-E	2.5	0	1.13	1.39	1.18	1.58	1.16	1.49	94	120
6286-F	5.0	0	1.06	1.20	1.11	1.81	1.09	1.51	88	122
6286-G	7.5	0	1.11	1.19	1.30	1.40	1.21	1.30	98	105
6286-H	10.0	0	1.02	1.24	1.58	1.62	1.30	1.43	105	115
6288-E	5.0	1.0	1.24	1.29	1.40	1.53	1.32	1.41	106	114
6288-F	5.0	2.0	1.16	1.45	0.83	1.25	1.00	1.35	81	109
6288-G	5.0	3.0	1.11	1.18	1.16	1.53	1.14	1.36	92	110
6288-H	5.0	4.0	1.20	1.40	1.18	1.40	1.19	1.40	96	113

TABLE 12. *Dry weight, expressed as grams per ten plants, obtained from the absolute control cultures supplied with nutrient solution of pH = 4.0.*

TREATMENT		CULTURE 1		CULTURE 2		CULTURE 3		AVERAGE	RELATIVE AVERAGE
Fe p.p.m.	Mn p.p.m.	Pot 1	Pot 2	Pot 1	Pot 2	Pot 1	Pot 2		
4.0	0.5	0.93	0.93	1.38	1.82	1.14	1.26	1.24	100
0	0.5	0.97	1.02	1.43	1.43	1.54	1.45	1.31	105
4.0	0	1.09	0.91	1.16	1.13	1.09	1.13	1.09	88
0	0	0.55	0.55	1.24	1.20	1.36	1.35	1.04	84

TABLE 13. [*See p. 24.*]

TABLE 14. *Dry weight, expressed as grams per ten plants, obtained from the absolute control cultures supplied with nutrient solution of pH = 5.0.*

TREATMENT		CULTURE 1		CULTURE 2		CULTURE 3		AVERAGE	RELATIVE AVERAGE
Fe p.p.m.	Mn p.p.m.	Pot 1	Pot 2	Pot 1	Pot 2	Pot 1	Pot 2		
4.0	0.5	2.96	2.50	3.17	3.32	2.94	2.77	2.94	100
0	0.5	1.29	1.37	1.26	1.59	1.40	1.58	1.42	48
4.0	0	2.12	1.97	2.05	1.87	2.67	2.62	2.22	76
0	0	1.30	1.32	1.20	0.97	1.86	1.79	1.41	48

TABLE 15. [*See p. 25.*]

TABLE 16. *Dry weight, expressed as grams per ten plants, obtained from the absolute control cultures supplied with nutrient solution of pH = 6.0.*

TREATMENT		CULTURE 1		CULTURE 2		CULTURE 3		AVERAGE	RELATIVE AVERAGE
Fe p.p.m.	Mn p.p.m.	Pot 1	Pot 2	Pot 1	Pot 2	Pot 1	Pot 2		
4.0	0.5	3.14	3.32	3.46	3.92	3.49	3.54	3.48	100
0	0.5	3.43	3.02	2.15	2.44	3.78	3.89	3.12	90
4.0	0	3.38	3.26	3.44	3.20	.....	.....	3.32	95
0	0	2.24	2.73	3.23	3.00	2.20	2.58	2.66	76

TABLE 13. *Dry weight, expressed as grams per ten plants, obtained from the frits and their corresponding quartz control cultures supplied with nutrient solution of pH = 5.0.*

FRIT			DRY WEIGHT PER 10 PLANTS							
No.	Composition (percent)		Culture 1		Culture 2		Average		Percentage of the absolute control plants receiving Fe and Mn	
	Fe_2O_3	MnO_2	Quartz	Frit	Quartz	Frit	Quartz	Frit	Quartz	Frit
6285-A	2.5	0	1.38	3.94	2.26	3.62	1.82	3.78	62	129
6285-B	5.0	0	2.14	3.21	2.70	3.97	2.42	3.59	82	122
6285-C	7.5	0	2.43	3.31	2.08	3.75	2.26	3.53	77	120
6285-D	10.0	0	3.19	3.97	2.68	3.71	2.94	3.84	100	131
6287-A	5.0	1.0	2.81	3.47	1.47	3.94	2.14	3.71	73	126
6287-B	5.0	2.0	3.17	4.07	3.96	5.03	3.56	4.70	121	160
6287-C	5.0	3.0	2.74	4.60	2.90	3.87	2.82	4.24	96	144
6287-D	5.0	4.0	2.40	4.05	2.33	4.28	2.37	4.17	81	142
6286-E	2.5	0	2.39	2.68	1.69	2.79	2.04	2.74	69	93
6286-F	5.0	0	2.00	2.65	2.00	3.11	2.00	2.88	68	98
6286-G	7.5	0	1.43	2.56	1.89	3.15	1.66	2.86	56	97
6286-H	10.0	0	1.91	2.74	2.15	3.25	2.03	3.00	69	102
6288-E	5.0	1.0	1.67	2.59	1.80	3.15	1.74	2.87	59	98
6288-F	5.0	2.0	1.46	2.71	1.50	2.53	1.48	2.62	50	89
6288-G	5.0	3.0	1.39	2.07	2.20	3.41	1.80	2.74	61	93
6288-H	5.0	4.0	1.49	2.63	1.59	3.17	1.54	2.90	52	99

TABLE 15. *Dry weight, expressed as grams per ten plants, obtained from the frits and their corresponding quartz control cultures supplied with nutrient solution of pH = 6.0.*

FRIT			DRY WEIGHT PER 10 PLANTS							
No.	Composition (percent)		Culture 1		Culture 2		Average		Percentage of the absolute control plants receiving Fe and Mn	
	Fe_2O_3	MnO_2	Quartz	Frit	Quartz	Frit	Quartz	Frit	Quartz	Frit
6585-A	2.5	0	4.15	4.95	3.51	5.68	3.83	5.32	110	153
6285-B	5.0	0	4.23	5.97	3.30	5.02	3.77	5.50	108	158
6285-C	7.5	0	3.95	6.93	2.75	5.52	3.35	6.23	96	179
6285-D	10.0	0	3.25	4.95	4.03	5.68	3.64	5.32	105	153
6287-A	5.0	1.0	2.92	4.36	3.18	5.55	3.05	4.96	88	143
6287-B	5.0	2.0	3.19	6.28	4.76	8.47	3.98	7.38	114	212
6287-C	5.0	3.0	3.64	5.76	3.15	5.08	3.40	5.42	98	156
6287-D	5.0	4.0	3.27	4.03	3.05	4.17	3.16	4.10	91	118
6286-E	2.5	0	2.77	3.83	4.05	4.95	3.41	4.39	98	126
6286-F	5.0	0	2.00	3.81	3.68	4.34	2.84	4.08	82	117
6286-G	7.5	0	1.95	3.90	3.14	4.49	2.55	4.20	73	121
6286-H	10.0	0	1.51	2.88	3.38	4.24	2.45	3.56	70	102
6288-F	5.0	1.0	3.49	4.70	4.23	5.28	3.86	4.99	111	143
6288-F	5.0	2.0	2.77	3.52	.....	.....	2.77	3.52	80	101
6288-G	5.0	3.0	3.17	3.55	2.90	4.54	3.04	4.05	87	116
6288-H	5.0	4.0	2.93	3.44	2.84	4.83	2.89	4.14	83	119

TABLE 17. *Dry weight, expressed as grams per ten plants, obtained from the frits and their corresponding quartz control cultures supplied with nutrient solution of pH = 7.0.*

FRIT			DRY WEIGHT PER 10 PLANTS							
No.	Composition (percent)		Culture 1		Culture 2		Average		Percentage of the absolute control plants receiving Fe and Mn	
	Fe_2O_3	MnO_2	Quartz	Frit	Quartz	Frit	Quartz	Frit	Quartz	Frit
6285-A	2.5	0	0.78	1.83	0.89	1.79	0.84	1.81	72	155
6285-B	5.0	0	1.03	1.81	0.73	1.77	0.83	1.79	71	153
6285-C	7.5	0	0.95	1.69	0.79	1.17	0.87	1.43	74	122
6285-D	10.0	0	0.80	1.56	0.97	1.66	0.89	1.61	76	138
6287-A	5.0	1.0	1.18	1.95	0.86	2.16	1.02	2.06	87	176
6287-B	5.0	2.0	1.10	1.88	1.00	1.86	1.05	1.87	90	160
6287-C	5.0	3.0	1.05	1.49	0.95	1.84	1.00	1.67	85	143
6287-D	5.0	4.0	0.98	1.73	1.14	1.74	1.06	1.74	91	149
6286-E	2.5	0	0.83	1.16	0.83	1.42	0.83	1.29	71	110
6286-F	5.0	0	0.74	1.05	0.92	1.34	0.83	1.20	71	102
6286-G	7.5	0	0.73	1.22	0.77	1.36	0.75	1.29	64	110
6286-H	10.0	0	0.76	1.26	0.86	1.44	0.81	1.35	69	115
6288-E	5.0	1.0	0.73	1.25	0.84	1.44	0.79	1.35	68	115
6288-F	5.0	2.0	0.97	1.18	0.78	1.59	0.88	1.39	75	118
6288-G	5.0	3.0	0.86	1.23	0.89	1.61	0.88	1.42	75	121
6288-H	5.0	4.0	0.74	1.37	0.84	1.58	0.79	1.48	68	126

TABLE 18. *Dry weight, expressed as grams per ten plants, obtained from the absolute control cultures supplied with nutrient solution of pH = 7.0.*

TREATMENT		CULTURE 1		CULTURE 2		CULTURE 3		AVERAGE	RELATIVE AVERAGE
Fe p.p.m.	Mn p.p.m.	Pot 1	Pot 2	Pot 1	Pot 2	Pot 1	Pot 2		
4.0	0.5	1.03	1.03	1.36	1 28	1.17	1.17	1.17	100
0	0.5	0.93	0.89	0.73	0.63	1.09	1.00	0.88	75
4.0	0	1.38	1.26	1.05	0.98	1.58	1.64	1.31	112
0	0	..82	0.83	0.73	0.71	1.26	1.32	0.95	81

The effect of the pH value of the nutrient solution on the relative difference in the dry weights of the plants grown in frit and in corresponding control cultures was demonstrated by figure 11. The same relative differences were obtained for the dry weights as for the fresh weights of the plants.

D. ABSORPTION OF IRON BY THE PLANTS

1. Concentration of iron in the dry material

Surface contamination of the plants by dust may have been a major source of error in iron determination performed on the dry material. Unfortunately, this error was not fully recognized until the analyses of the samples obtained from the two first experiments had been completed. In order to eliminate this source of error, the plants of the third experiment (pH = 4.0) were washed by repeated dipping in distilled water after they had been harvested. Somewhat more consistent data were obtained. A still higher degree of consistency was obtained, however, in the last experiment (pH = 5.0) in which the plants were dipped several times in a dilute hydrochloric acid solution and rinsed in distilled water before being placed in the drying oven.

Nutrient solution maintained at pH = 4.0: The iron contents expressed as parts per million of the oven-dry material are listed in tables 19 and 20. The data show that the plants grown in frit contained more iron per unit of dry material than those grown in their corresponding control cultures. The data also indicate that the amount of iron present in the frit did not influence the concentration of iron in the dry material of the plants, nor was there any evidence that the differences of the manganese content of the frit affected the amounts in the plants.

As shown by the data in table 20, the addition of soluble iron to the nutrient solution had but little influence upon the concentration of iron in the dry matter of the plants grown in the *absolute* control cultures. When manganese but no iron had been added to the solution, a slight depression of the concentration of iron was observed in the the dry plant material.

TABLE 19. *Iron content, expressed as parts per million, in the oven dry material, grown in frits and their corresponding quartz control cultures supplied with nutrient solution of pH = 4.0.*

FRIT			PARTS PER MILLION OF IRON IN DRY MATERIAL		
No.	Composition (percent)		Culture 1	Culture 2	Average
	Fe_2O_3	MnO_2			
6285-A	2.5	0	151	75	113
control			52	88	70
6285-B	5.0	0	113	81	97
control			108	80	94
6285-C	7.5	0	99	83	91
control			115	71	93
6285-D	10.0	0	85	69	77
control			86	69	78
6287-A	5.0	1.0	77	75	76
control			83	94	89
6287-B	5.0	2.0	106	79	93
control			103	91	97
6287-C	5.0	3.0	90	71	81
control			106	79	93
6287-D	5.0	4.0	82	88	85
control			88	88	88
6286-E	2.5	0	89	96	93
control			85	85	85
6286-F	5.0	0	81	75	78
control			106	88	97
6286-G	7.5	0	90	46	68
control			93	78	86
6286-H	10.0	0	95	82	89
control			95	84	90
6288-E	5.0	1.0	107	88	98
control			111	85	98
6288-F	5.0	2.0	90	94	92
control			72	116	94
6288-G	5.0	3.0	38	76	57
control			92	62	77
6288-H	5.0	4.0	96	80	88
control			103	62	83

TABLE 20. *Iron content, expressed as parts per million, in the oven dry material, grown in the absolute control cultures supplied with nutrient solution at pH = 4.0.*

TREATMENT		CULTURE 1		CULTURE 2		CULTURE 3		AVERAGE
Fe p.p.m.	Mn p.p.m.	Pot 1	Pot 2	Pot 1	Pot 2	Pot 1	Pot 2	
4.0	0.5	95	87	99	88	91	97	93
0	0.5	75	72	....	75	81	72	75
4.0	0	98	91	83	....	114	97	97
0	0	110	79	75	83	105	97	92

TABLE 21. *Iron content, expressed as parts per million, in the oven dry material, grown in the frits and their corresponding quartz control cultures supplied with nutrient solution at pH = 5.0.*

FRIT			PARTS PER MILLION OF IRON IN DRY MATERIAL		
No.	Composition (percent)		Culture 1	Culture 2	Average
	Fe_2O_3	MnO_2			
6285-A	2.5	0	84	81	83
control			57	94	76
6285-B	5.0	0	73	76	75
control			53	75	64
6285-C	7.5	0	71	115	93
control			81	65	73
6285-D	10.0	0	79	77	78
control			62	56	59
6287-A	5.0	1.0	108	92	100
control			62	95	79
6287-B	5.0	2.0	82	111	97
control			81	87	84
6287-C	5.0	3.0	95	112	104
control			69	96	83
6287-D	5.0	4.0	87	117	102
control			71	128	100
6286-E	2.5	0	47	84	66
control			39	75	57
6286-F	5.0	0	69	62	66
control			56	56	56
6286-G	7.5	0	60	75	68
control			51	74	63
6286-H	10.0	0	79	67	73
control			76	57	67
6288-E	5.0	1.0	77	87	82
control			65	62	64
6288-F	5.0	2.0	71	85	78
control			63	79	71
6288-G	5.0	3.0	92	90	91
control			75	94	85
6288-H	5.0	4.0	93	100	97
control			75	80	78

TABLE 22. *Iron content, expressed as parts per million, in the oven dry material, grown in the absolute control cultures supplied with nutrient solution at pH = 5.0.*

TREATMENT		CULTURE 1		CULTURE 2		CULTURE 3		AVERAGE
Fe p.p.m.	Mn p.p.m.	Pot 1	Pot 2	Pot 1	Pot 2	Pot 1	Pot 2	
4.0	0.5	69	75	91	75	75	71	76
0	0.5	77	58	56	52	73	61	63
4.0	0	85	75	115	109	71	74	88
0	0	46	42	101	91	81	81	74

TABLE 23. *Iron content, expressed as parts per million, in the oven dry material, grown in the frits and their corresponding quartz control cultures supplied with nutrient solution at pH = 6.0.*

FRIT			PARTS PER MILLION OF IRON IN DRY MATERIAL		
No.	Composition (percent)		Culture 1	Culture 2	Average
	Fe_2O_3	MnO_2			
6285-A	2.5	0	168	145	157
control			130	146	138
6285-B	5.0	0	144	180	162
control			122	155	136
6285-C	7.5	0	129	162	146
control			106	167	137
6285-D	10.0	0	140	162	151
control			134	152	143
6287-A	5.0	1.0	165	147	156
control			164	162	163
6287-B	5.0	2.0	135	121	128
control			165	137	151
6287-C	5.0	3.0	167	137	152
			162	130	146
6287-D	5.0	4.0	150	150	150
control			140	150	145
6286-E	2.5	0	96	202	150
control			125	175	150
6286-F	5.0	0	145	160	153
control			136	152	144
6286-G	7.5	0	157	221	188
control			147	141	144
6286-H	10.0	0	160	141	150
control			155	157	156
6288-E	5.0	1.0	151	157	154
control			127	184	156
6288-F	5.0	2.0	175	....	175
control			179	....	179
6288-G	5.0	3.0	187	154	171
control			121	154	138
6288-H	5.0	4.0	132	147	140
control			111	155	133

TABLE 24. *Iron content, expressed as parts per million, in the oven dry material, grown in the absolute control cultures supplied with nutrient solution at pH = 6.0.*

TREATMENT		CULTURE 1		CULTURE 2		CULTURE 3		AVERAGE
Fe p.p.m.	Mn p.p.m.	Pot 1	Pot 2	Pot 1	Pot 2	Pot 1	Pot 2	
4.0	0.5	143	148	163	136	125	125	140
0	0.5	155	157	181	162	167	140	160
4.0	0	165	123	95	177	....	....	140
0	0	158	132	132	115	151	282	162

TABLE 25. *Iron content, expressed as parts per million, in the oven dry material, grown in the frits and their corresponding quartz control cultures supplied with nutrient solution at pH = 7.0.*

FRIT			PARTS PER MILLION OF IRON IN DRY MATERIAL		
No.	Composition (percent)		Culture 1	Culture 2	Average
	Fe_2O_3	MnO_2			
6285-A	2.5	0	158	155	157
control			200	115	158
6285-B	5.0	0	235	122	179
control			225	116	171
6285-C	7.5	0	218	129	174
control			253	131	192
6285-D	10.0	0	265	131	198
control			160	104	132
6287-A	5.0	1.0	165	111	139
control			128	122	125
6287-B	5.0	2.0	123	89	106
control			124	112	118
6287-C	5.0	3.0	113	110	112
control			130	105	118
6287-D	5.0	4.0	133	130	132
control			132	132	132
6286-E	2.5	0	130	105	118
control			150	272	211
6286-F	5.0	0	145	241	193
control			145	245	195
6286-G	7.5	0	131	250	191
control			167	240	204
6286-H	10.0	0	137	225	181
control			135	132	134
6288-E	5.0	1.0	132	112	122
control			127	120	124
6288-F	5.0	2.0	155	104	129
control			199	146	173
6288-G	5.0	3.0	150	160	155
control			162	126	144
6288-H	5.0	4.0	250	131	191
control			127	207	167

TABLE 26. *Iron content, expressed as parts per million, in the oven dry material, grown in the absolute control cultures supplied with nutrient solution at pH = 7.0.*

TREATMENT		CULTURE 1		CULTURE 2		CULTURE 3		AVERAGE
Fe p.p.m.	Mn p.p.m.	Pot 1	Pot 2	Pot 1	Pot 2	Pot 1	Pot 2	
4.0	0.5	187	159	122	131	121	120	140
0	0.5	152	157	128	132	137	145	142
4.0	0	122	144	122	126	126	127	128
0	0	140	120	149	140	156	157	144

TABLE 27. *Total iron absorbed, expressed as milligrams per ten plants, grown in the frits, their corresponding quartz control cultures, and the absolute control cultures supplied with nutrient solution at pH = 4.0.*

FRIT			MILLIGRAMS IRON ABSORBED PER 10 PLANTS					
No.	Composition (percent)		Culture 1		Culture 2		Average	
	Fe_2O_3	MnO_2	Quartz	Frit	Quartz	Frit	Quartz	Frit
6285-A	2.5	0	0.07	0.26	0.12	0.13	0.10	0.20
6285-B	5.0	0	0.14	0.16	0.12	0.13	0.13	0.15
6285-C	7.5	0	0.18	0.20	0.08	0.13	0.13	0.17
6285-D	10.0	0	0.10	0.15	0.08	0.11	0.09	0.13
6287-A	5.0	1.0	0.14	0.13	0.14	0.12	0.14	0.13
6287-B	5.0	2.0	0.14	0.19	0.12	0.12	0.13	0.16
6287-C	5.0	3.0	0.15	0.16	0.10	0.12	0.13	0.14
6287-D	5.0	4.0	0.13	0.14	0.12	0.14	0.13	0.14
6286-E	2.5	0	....	0.12	0.10	0.15	0.10	0.14
6286-F	5.0	0	0.11	0.10	0.10	0.14	0.11	0.13
6286-G	7.5	0	0.10	0.11	0.10	0.06	0.10	0.09
6286-H	10.0	0	0.10	0.12	0.13	0.13	0.12	0.13
6288-E	5.0	1.0	0.14	0.14	0.12	0.13	0.13	0.14
6288-F	5.0	2.0	0.08	0.13	0.09	0.12	0.09	0.13
6288-G	5.0	3.0	0.10	0.04	0.07	0.12	0.09	0.08
6288-H	5.0	4.0	0.12	0.13	0.07	0.11	0.10	0.12

Absolute control cultures

TREATMENT		CULTURE 1		CULTURE 2		CULTURE 3		AVERAGE
Fe (p.p.m.)	Mn (p.p.m.)	Pot 1	Pot 2	Pot 1	Pot 2	Pot 1	Pot 2	
4.0	0.5	0.09	0.08	0.14	0.16	0.10	0.12	0.12
0	0.5	0.07	0.07	....	0.11	0.12	0.10	0.09
4.0	0	0.11	0.08	0.09	....	0.12	0.11	0.10
0	0	0.06	0.04	0.09	0.11	0.14	0.13	0.10

Nutrient solution maintained at pH = 5.0: The parts per million of iron in the oven-dry plant material produced by cultures maintained at pH = 5.0 are listed in tables 21 and 22. Even though there were large differences in the results obtained from duplicate cultures, a consistently higher average value was obtained for the plants grown in frit than for those grown in their corresponding control cultures. Figure 12 indicates that the frit series 6285 produced plants containing higher concentrations of iron than the frit series 6286. Similarly, the frit series 6287 produced plants with a higher concentration of iron in the dry matter than the frit series 6288. A close parallelism between the concentrations of iron in the plants grown in the frits

and in their corresponding control cultures was observed for both of the frit series containing iron but no manganese.

From figure 12 it is seen that the presence of manganese in the frits increased the concentrations of iron in the dry matter of the plants.

TABLE 28. *Total iron absorbed, expressed as milligrams per ten plants, grown in the frits, their corresponding quartz control cultures, and the absolute control cultures supplied with nutrient solution at pH = 5.0.*

FRIT			MILLIGRAMS IRON ABSORBED PER 10 PLANTS					
No.	Composition (percent)		Culture 1		Culture 2		Average	
	Fe_2O_3	MnO_2	Quartz	Frit	Quartz	Frit	Quartz	Frit
6285-A	2.5	0	0.08	0.33	0.21	0.29	0.16	0.31
6285-B	5.0	0	0.11	0.23	0.20	0.30	0.16	0.27
6285-C	7.5	0	0.20	0.24	0.14	0.43	0.17	0.34
6285-D	10.0	0	0.20	0.31	0.15	0.29	0.18	0.30
6287-A	5.0	1.0	0.17	0.37	0.14	0.36	0.16	0.37
6287-B	5.0	2.0	0.26	0.36	0.34	0.56	0.30	0.46
6287-C	5.0	3.0	0.19	0.44	0.28	0.43	0.24	0.44
6287-D	5.0	4.0	0.17	0.35	0.28	0.50	0.23	0.43
6286-E	2.5	0	0.09	0.13	0.13	0.23	0.11	0.18
6286-F	5.0	0	0.11	0.18	0.11	0.19	0.11	0.19
6286-G	7.5	0	0.07	0.15	0.14	0.24	0.11	0.20
6286-H	10.0	0	0.15	0.22	0.12	0.22	0.14	0.22
6288-E	5.0	1.0	0.11	0.20	0.11	0.27	0.11	0.24
6288-F	5.0	2.0	0.09	0.19	0.12	0.22	0.11	0.21
6288-G	5.0	3.0	0.10	0.19	0.21	0.31	0.16	0.25
6288-H	5.0	4.0	0.11	0.24	0.13	0.32	0.12	0.28

Absolute control cultures

TREATMENT		CULTURE 1		CULTURE 2		CULTURE 3		AVERAGE
Fe (p.p.m.)	Mn (p.p.m.)	Pot 1	Pot 2	Pot 1	Pot 2	Pot 1	Pot 2	
4.0	0.5	0.20	0.19	0.29	0.25	0.22	0.20	0.23
0	0.5	0.10	0.08	0.07	0.08	0.10	0.10	0.09
4.0	0	0.18	0.15	0.24	0.20	0.19	0.19	0.19
0	0	0.06	0.06	0.12	0.09	0.15	0.14	0.10

This result is not consistent with the general belief that manganese exerts a depressing effect on the absorption of iron by plants. However, such a depressive effect of manganese is demonstrated by the data presented in table 22, from which it is seen that when both iron and

manganese were added to the nutrient solution of the *absolute* control cultures, the concentration of iron in the dry matter of the plants was less than when only iron was added. Similarly when only manganese

TABLE 29. *Total iron absorbed, expressed as milligrams per ten plants, grown in the frits, their corresponding quartz control cultures, and the absolute control cultures supplied with a nutrient solution at pH = 6.0.*

FRIT			MILLIGRAMS IRON ABSORBED PER 10 PLANTS					
No.	Composition (percent)		Culture 1		Culture 2		Average	
	Fe_2O_3	MnO_2	Quartz	Frit	Quartz	Frit	Quartz	Frit
6285-A	2.5	0	0.54	0.84	0.52	0.82	0.53	0.83
6285-B	5.0	0	0.52	0.86	0.51	0.90	0.52	0.88
6285-C	7.5	0	0.42	0.89	0.46	0.90	0.44	0.90
6285-D	10.0	0	0.44	0.69	0.62	0.93	0.53	0.81
6287-A	5.0	1.0	0.48	0.72	0.52	0.82	0.50	0.77
6287-B	5.0	2.0	0.53	0.85	0.66	1.03	0.60	0.94
6287-C	5.0	3.0	0.59	0.97	0.41	0.70	0.50	0.84
6287-D	5.0	4.0	0.46	1.26	0.46	0.63	0.46	0.95
6286-E	2.5	0	0.35	0.37	0.71	1.00	0.53	0.69
6286-F	5.0	0	0.27	0.55	0.56	0.69	0.42	0.62
6286-G	7.5	0	0.29	0.62	0.44	....	0.37	0.62
6286-H	10.0	0	0.23	0.46	0.53	0.60	0.38	0.53
6288-E	5.0	1.0	0.45	0.71	0.78	0.83	0.63	0.77
6288-F	5.0	2.0	0.50	0.62	....	....	0.50	0.62
6288-G	5.0	3.0	0.39	0.67	0.45	0.70	0.42	0.69
6288-H	5.0	4.0	0.33	0.46	0.44	0.71	0.39	0.59

Absolute control cultures

TREATMENT		CULTURE 1		CULTURE 2		CULTURE 3		AVERAGE
Fe (p.p.m.)	Mn (p.p.m.)	Pot 1	Pot 2	Pot 1	Pot 2	Pot 1	Pot 2	
4.0	0.5	0.45	0.49	0.57	0.53	0.44	0.44	0.49
0	0.5	0.53	0.48	0.39	0.40	0.64	0.54	0.50
4.0	0	0.56	0.40	0.33	0.57	....	....	0.47
0	0	0.36	0.36	0.43	0.35	0.33	0.73	0.43

was added, the concentration of iron in the dry matter was less than when neither of these two nutrients was added.

Nutrient solution maintained at Ph = 6.0 and 7.0: As already mentioned, no precautions were taken to eliminate dust contamination of the material obtained in these experiments. It is seen from the

data in tables 23 to 26 inclusive that the iron contents of the dry material was of a higher order of magnitude than the corresponding data obtained from the previous experiments, and also that the differences between the duplicate cultures were generally very large. Therefore, no con-

TABLE 30. *Total iron absorbed, expressed as milligrams per ten plants, grown in the frits, their corresponding quartz control cultures, and the absolute control cultures supplied with nutrient solution at pH = 7.0.*

FRIT			MILLIGRAMS IRON ABSORBED PER 10 PLANTS					
No.	Composition (percent)		Culture 1		Culture 2		Average	
	Fe_2O_3	MnO_2	Quartz	Frit	Quartz	Frit	Quartz	Frit
6285-A	2.5	0	0.16	0.29	0.10	0.28	0.13	0.29
6285-B	5.0	0	0.23	0.43	0.09	0.22	0.16	0.33
6285-C	7.5	0	0.24	0.37	0.10	0.15	0.17	0.26
6285-D	10.0	0	0.13	0.41	0.10	0.22	0.12	0.32
6287-A	5.0	1.0	0.15	0.32	0.11	0.24	0.13	0.28
6287-B	5.0	2.0	0.14	0.23	0.11	0.17	0.12	0.20
6287-C	5.0	3.0	0.14	0.17	0.10	0.20	0.12	0.19
6287-D	5.0	4.0	0.13	0.23	0.15	0.23	0.14	0.23
6286-E	2.5	0	0.12	0.15	0.23	0.15	0.18	0.15
6286-F	5.0	0	0.11	0.15	0.23	0.32	0.17	0.24
6286-G	7.5	0	0.12	0.16	0.18	0.34	0.15	0.25
6286-H	10.0	0	0.10	0.17	0.11	0.32	0.11	0.25
6288-E	5.0	1.0	0.09	0.17	0.10	0.19	0.10	0.18
6288-F	5.0	2.0	0.19	0.18	0.11	0.17	0.15	0.18
6288-G	5.0	3.0	0.14	0.18	0.11	0.26	0.13	0.22
6288-H	5.0	4.0	0.09	0.34	0.17	0.21	0.13	0.28

Absolute control cultures

TREATMENT		CULTURE 1		CULTURE 2		CULTURE 3		AVERAGE
Fe (p.p.m.)	Mn (p.p.m.)	Pot 1	Pot 2	Pot 1	Pot 2	Pot 1	Pot 2	
4.0	0.5	0.19	0.16	0.17	0.17	0.14	0.14	0.16
0	0.5	0.14	0.15	0.09	0.09	0.15	0.15	0.13
4.0	0	0.17	0.18	0.13	0.12	0.20	0.21	0.17
0	0	0.11	0.10	0.11	0.10	0.20	0.21	0.14

clusion can be drawn as to the relative concentrations of iron in the plant material grown in these experiments.

2. *Total iron absorbed by the plants*

Nutrient solution maintained at pH = 4.0: Although the concentration of iron in the dry matter of the plants grown in the frits and

TABLE 31. *Manganese content, expressed as parts per million, in the oven dry material, grown in the frits and their corresponding quartz control cultures supplied with nutrient solution at pH = 4.0.*

FRIT			PARTS PER MILLION MANGANESE IN DRY MATERIAL		
No.	Composition (percent)		Culture 1	Culture 2	Average
	Fe_2O_3	MnO_2			
6285-A	2.5	0	186	162	174
control			173	154	164
6285-B	5.0	0	154	160	157
control			139	133	136
6285-C	7.5	0	146	159	153
control			130	174	152
6285-D	10.0	0	128	135	132
control			130	128	129
6287-A	5.0	1.0	261	270	266
control			303	320	312
6287-B	5.0	2.0	347	302	325
control			297	312	305
6287-C	5.0	3.0	311	367	339
control			288	417	353
6287-D	5.0	4.0	342	366	354
control			418	404	411
6286-E	2.5	0	120	124	122
control			135	118	127
6286-F	5.0	0	116	121	119
control			136	121	129
6286-G	7.5	0	121	142	132
control			131	159	145
6286-H	10.0	0	118	121	120
control			118	148	133
6288-E	5.0	1.0	156	194	175
control			112	159	136
6288-F	5.0	2.0	227	213	220
control			212	192	202
6288-G	5.0	3.0	244	250	247
control			273	226	250
6288-H	5.0	4.0	196	265	231
control			215	278	247

and in their corresponding control cultures did not show significant differences, as described above, the total amount absorbed by the plants was greater for the frit-borne plants than for their corresponding control plants as is shown by the data in table 27. The plants grown in the frits of the 6285 and 6287 series absorbed more iron than the plants grown in the frits of the 6286 and 6288 series. Further, the control plants corresponding to the 6285 and 6287 frit series absorbed more iron than the control plants corresponding to the 6286 and 6288 frit series. The average amounts of iron absorbed by the plants grown in the *absolute* control cultures receiving complete nutrient solution was less than that absorbed by the frit-grown plants in most instances.

Nutrient solution maintained at pH = 50: At pH = 50 of the nutrient solution, it was found that higher concentrations of iron existed in the dry matter of the plants grown in the frits than in their corresponding control cultures. The total amounts of iron absorbed by the plants in the various cultures are listed in table 28. The average

TABLE 32. *Manganese content, expressed as parts per million, in the oven dry material grown in the absolute control cultures supplied with nutrient solution at pH = 4.0.*

TREATMENT		CULTURE 1		CULTURE 2		CULTURE 3		AVERAGE
Fe (p.p.m.)	Mn (p.p.m.)	Pot 1	Pot 2	Pot 1	Pot 2	Pot 1	Pot 2	
4.0	0.5	132	128	126	138	....	....	131
0	0.5	138	144	195	213	209	195	182
4.0	0	trace[1]	trace	trace	trace	trace	trace	trace
0	0	trace	trace	trace	trace	trace	trace	trace

[1]Less than 10 parts per million.

values were plotted against the frit compositions in figure 12. It was noticed that the plants grown in the frit cultures absorbed about twice as much iron as the plants in their corresponding control cultures. This was true for all four series of frits. It also is evident from the data assembled in table 28 that the plants grown in the frits of the grown in the *absolute* control cultures receiving a complete nutrient solution.

Nutrient solution maintained at pH = 6.0 and 7.0: The data presented in tables 29 and 30 show that there was a greater absorption of iron by the plants grown in the frits than by those grown in their corresponding control cultures. These differences are especially noticeable for the frit series 6285 and 6287.

3. *Summary*

The data obtained for the absorption of iron by plants grown in nutrient solutions maintained at pH = 5.0 are the most reliable since precautions were taken to eliminate dust contaminations of the plant material. The results of this experiment may be summarized as follows:

1. The plants grown in the frit cultures accumulated more iron in their tissues than the plants grown in their corresponding control cultures. These results indicate that the frit-grown plants had a better access to available iron than the corresponding control plants.

2. The plants grown in the frits of the 6285 and 6287 frit series absorbed more iron than the plants grown in the 6286 and 6288 frit series.

3. The control plants corresponding to the 6285 and 6287 frit series generally absorbed more iron than the control plants corresponding to the 6286 and 6288 frit series. This indicates that the iron in the former frits was slightly more soluble than in the latter.

4. There was no correlation between the amount of iron in the frit and the amount absorbed by the plants.

E. ABSORPTION OF MANGANESE BY THE PLANTS

1. Concentration of manganese in the dry material

Nutrient solution maintained at pH = 4.0: The manganese contents of the dry plant material expressed as part per million were listed in tables 31 and 32. It was evident from these data that the presence of manganese in the frits exerted a considerable influence upon the concentration of manganese in the plant tissue. An increase in the manganese dioxide content from 1.0 to 4.0 percent in the frit increased correspondingly the concentration of manganese in the plants.

The concentrations of manganese in the dry matter of the corresponding control plants were of the same order of magnitude as in the frit-grown plants. This situation indicated a relatively high solubility of the manganese in the frit for otherwise it could not have reached the control plants.

The plants grown in the 6287 frit series contained higher concentrations of manganese than the plants grown in the 6288 frit series. The solubility of the manganese in the 6287 frits, apparently was greater than in the 6288 frits.

The *absolute* control plants supplied with a nutrient solution from which manganese was excluded did not contain detectable amounts of manganese.

Nutrient solution maintained at pH = 5.0: The manganese contents of the oven-dry plants grown in solutions maintained at pH = 5.0 are listed in tables 33 and 34. The data again show increased manganese concentrations in the dry material as the percentages of manganese in the frits were increased. In contrast to the data from the previous experiments, large differences were observed in the plants grown in the frits and in their corresponding control cultures.

In both iron frits (series 6285 and 6286) the corresponding control plants contained higher concentrations of manganese than the frit-grown plants. The same large differences in the concentrations of manganese in the dry plant material were observed in the frit-borne and in their corresponding control plants of the manganese frit series 6287. No such differences were observed with respect to the frit series 6288. These results, together with the relatively low manganese concentrations of the plants grown in this frit, again indicate that the

TABLE 33. *Manganese content, expressed as parts per million, in the oven dry material, grown in the frits and their corresponding quartz control cultures supplied with nutrient solution at Ph = 5.0.*

FRIT			PARTS PER MILLION MANGANESE IN DRY MATERIAL		
No.	Composition (percent)		Culture 1	Culture 2	Average
	Fe_2O_3	MnO_2			
6285-A	2.5	0	145	137	141
control			248	216	232
6285-B	5.0	0	154	127	141
control			210	204	207
6285-C	7.5	0	130	141	136
control			214	218	216
6285-D	10.0	0	128	127	128
control			205	213	209
6287-A	5.0	1.0	142	235	189
control			393	388	390
6287-B	5.0	2.0	213	205	209
control			280	293	287
6287-C	5.0	3.0	224	222	223
control			417	382	400
6287-D	5.0	4.0	297	243	270
control			481	419	450
6286-E	2.5	0	186	218	202
control			255	272	264
6286-F	5.0	0	191	213	202
control			281	271	276
6286-G	7.5	0	193	201	297
control			299	290	295
6286-H	10.0	0	183	195	189
control			254	293	273
6288-E	5.0	1.0	116	85	101
control			93	68	81
6288-F	5.0	2.0	146	111	128
control			120	88	104
6288-G	5.0	3.0	117	177	147
control			196	155	176
6288-H	5.0	4.0	239	205	222
control			185	215	200

TABLE 34. *Manganese content, expressed as parts per million, in the oven dry material, grown in the absolute control cultures supplied with nutrient solution at pH = 5.0.*

TREATMENT		CULTURE 1		CULTURE 2		CULTURE 3		AVERAGE
Fe (p.p.m.)	Mn (p.p.m.)	Pot 1	Pot 2	Pot 1	Pot 2	Pot 1	Pot 2	
4.0	0.5	212	212	191	196	213	201	204
0	0.5	316	322	358	344	341	342	337
4.0	0	trace[1]	trace	trace	trace	trace	trace	trace
0	0	trace	trace	trace	trace	trace	trace	trace

[1]Less than 10 parts per million.

TABLE 35. *Manganese content, expressed as parts per million, in the oven dry material, grown in the frits and their corresponding quartz control cultures supplied with nutrient solution at pH = 6.0.*

FRIT			PARTS PER MILLION MANGANESE IN DRY MATERIAL		
No.	Composition (percent)		Culture 1	Culture 2	Average
	Fe_2O_3	MnO_2			
6285-A	2.5	0	78	75	77
control			109	123	116
6285-B	5.0	0	59	81	70
control			104	126	115
6285-C	7.5	0	68	80	74
control			137	156	147
6285-D	10.0	0	78	94	86
control			138	136	137
6287-A	5.0	1.0	146	180	163
control			245	348	297
6287-B	5.0	2.0	194	163	169
control			355	348	352
6287-C	5.0	3.0	209	194	202
control			292	420	356
6287-D	5.0	4.0	223	217	220
control			298	411	355
6286-E	2.5	0	150	112	131
control			198	135	167
6286-F	5.0	0	178	120	148
control			217	152	185
6286-G	7.5	0	153	99	126
control			239	180	210
6286-H	10.0	0	122	128	125
control			197	176	187
6288-E	5.0	1.0	112	84	98
control			88	98	93
6288-F	5.0	2.0	151	....	151
control			172	....	172
6288-G	5.0	3.0	201	217	209
control			203	220	212
6288-H	5.0	4.0	219	214	217
control			251	254	253

TABLE 36 *Manganese content, expressed as parts per million, in the oven dry material, grown in the absolute control cultures supplied with nutrient solution at pH = 6.0.*

TREATMENT		CULTURE 1		CULTURE 2		CULTURE 3		AVERAGE
Fe (p.p.m.)	Mn (p.p.m.)	Pot 1	Pot 2	Pot 1	Pot 2	Pot 1	Pot 2	
4.0	0.5	120	132	106	117	117	130	120
0	0.5	194	194	195	198	170	143	182
4.0	0	trace[1]	trace	trace	trace	trace	trace	trace
0	0	trace	trace	trace	trace	trace	14	trace

[1]Less than 10 parts per million.

TABLE 37. *Manganese content, expressed as parts per million, in the oven dry material, grown in the frits and their corresponding quartz control cultures supplied with nutrient solution at pH. = 7.0.*

FRIT			PARTS PER MILLION MANGANESE IN DRY MATERIAL		
No.	Composition (percent)		Culture 1	Culture 2	Average
	Fe_2O_3	MnO_2			
6285-A	2.5	0	39	83	61
control			122	118	120
6285-B	5.0	0	66	91	79
control			99	107	103
6285-C	7.5	0	139	99	119
control			50	138	94
6285-D	10.0	0	52	92	72
control			55	89	72
6287-A	5.0	1.0	136	166	151
control			170	168	169
6287-B	5.0	2.0	163	163	163
control			269	249	260
6287-C	5.0	3.0	176	190	183
control			276	350	214
6287-D	5.0	4.0	227	204	216
control			347	327	338
6286-E	2.5	0	134	100	118
control			170	170	170
6286-F	5.0	0	147	154	151
control			220	181	201
6286-G	7.5	0	115	134	125
control			199	181	190
6286-H	10.0	0	103	136	120
control			184	190	187
6288-E	5.0	1.0	113	37	75
control			79	35	58
6288-F	5.0	2.0	132	74	103
control			117	66	92
6288-G	5.0	3.0	174	248	211
control			160	85	128
6288-H	5.0	4.0	208	166	188
control			185	213	200

TABLE 38. *Manganese content, expressed as parts per million, in the oven dry material, grown in the absolute control cultures supplied with nutrient solution at pH = 7.0.*

TREATMENT		CULTURE 1		CULTURE 2		CULTURE 3		AVERAGE
Fe (p.p.m.)	Mn (p.p.m.)	Pot 1	Pot 2	Pot 1	Pot 2	Pot 1	Pot 2	
4.0	0.5	127	133	109	91	271	192	154
0	0.5	197	215	207	236	134	137	188
4.0	0	21	21	18	trace	trace	trace	trace
0	0	trace[1]	trace	21	14	trace	trace	trace

[1]Less than 10 parts per million.

manganese in the 6288 frits was less available to the plants than that in the 6287 frits. The data also indicate that the manganese in the 6288 frit was less soluble than in the 6287 frit since the control plants associated with the latter contain relatively large amounts of manganese.

TABLE 39. *Total manganese absorbed, expressed as milligrams per ten plants, grown in the frits, their corresponding quartz control cultures, and the absolute control cultures supplied with nutrient solution at pH = 4.0.*

FRIT			MILLIGRAMS MANGANESE ABSORBED PER 10 PLANTS					
No.	Composition (percent)		Culture 1		Culture 2		Average	
	Fe_2O_3	MnO_2	Quartz	Frit	Quartz	Frit	Quartz	Frit
6285-A	2.5	0	0.23	0.32	0.21	0.28	0.22	0.30
6285-B	5.0	0	0.18	0.21	0.19	0.26	0.19	0.24
6285-C	7.5	0	0.21	0.29	0.20	0.24	0.21	0.27
6285-D	10.0	0	0.15	0.23	0.16	0.22	0.16	0.23
6287-A	5.0	1.0	0.49	0.44	0.49	0.43	0.49	0.44
6287-B	5.0	2.0	0.41	0.62	0.43	0.44	0.42	0.53
6287-C	5.0	3.0	0.41	0.57	0.54	0.61	0.48	0.59
6287-D	5.0	4.0	0.60	0.57	0.55	0.57	0.58	0.57
6286-E	2.5	0	0.13	0.17	0.14	0.31	0.14	0.24
6286-F	5.0	0	0.14	0.14	0.13	0.22	0.14	0.18
6286-G	7.5	0	0.15	0.14	0.21	0.20	0.18	0.17
6286-H	10.0	0	0.12	0.15	0.23	0.20	0.18	0.18
6288-E	5.0	1.0	0.14	0.20	0.22	0.30	0.18	0.25
6288-F	5.0	2.0	0.25	0.33	0.16	0.27	0.20	0.30
6288-G	5.0	3.0	0.30	0.29	0.26	0.38	0.28	0.34
6288-H	5.0	4.0	0.26	0.27	0.33	0.37	0.30	0.32

Absolute control cultures

TREATMENT		CULTURE 1		CULTURE 2		CULTURE 3		AVERAGE
Fe (p.p.m.)	Mn (p.p.m.)	Pot 1	Pot 2	Pot 1	Pot 2	Pot 1	Pot 2	
4.0	0.5	0.12	0.12	0.17	0.25	....	....	0.17
0	0.5	0.13	0.15	0.28	0.30	0.32	0.28	0.28

Nutrient solution maintained at pH = 6.0 and 7.0: The manganese concentrations in the dry plant material produced at pH values of 6.0 and 7.0 are listed in tables 35 to 38 inclusive. The data from these experiments show the same general relationships as reported for the previous experiment. The observations already made regarding availability of manganese in the two frit series 6287 and 6288 were confirmed by these experiments.

2. *Total manganese absorbed by the plants*

The total amounts of manganese absorbed by the plants expressed as milligrams per ten plants, are listed in tables 39 to 42 inclusive. The average values were plotted against the compositions of the frits in figures 13 to 16 inclusive.

TABLE 40. *Total manganese absorbed, expressed as milligrams per ten plants, grown in the frits, their corresponding quartz control cultures, and the absolute control cultures supplied with nutrient solution at pH = 5.0.*

FRIT			MILLIGRAMS MANGANESE ABSORBED PER 10 PLANTS					
No.	Composition (percent)		Culture 1		Culture 2		Average	
	$F2_2O_3$	MnO_2	Quartz	Frit	Quartz	Frit	Quartz	Frit
6285-A	2.5	0	0.34	0.57	0.49	0.50	0.42	0.54
6285-B	5.0	0	0.45	0.49	0.55	0.50	0.50	0.50
6285-C	7.5	0	0.52	0.43	0.45	0.53	0.49	0.48
6285-D	10.0	0	0.65	0.51	0.57	0.47	0.61	0.49
6287-A	5.0	1.0	1.10	0.49	0.57	0.93	0.84	0.71
6287-B	5.0	2.0	0.89	0.93	1.16	1.03	1.03	0.98
6287-C	5.0	3.0	1.14	1.03	1.11	0.86	1.12	0.95
6287-D	5.0	4.0	1.15	1.20	0.98	1.04	1.07	1.12
6286-E	2.5	0	0.61	0.50	0.46	0.61	0.54	0.56
6286-F	5.0	0	0.56	0.51	0.54	0.66	0.55	0.59
6286-G	7.5	0	0.43	0.49	0.55	0.63	0.49	0.57
6286-H	10.0	0	0.49	0.50	0.63	0.63	0.56	0.57
6288-E	5.0	1.0	0.15	0.30	0.12	0.27	0.14	0.29
6288-F	5.0	2.0	0.18	0.40	0.13	0.28	0.16	0.34
6288-G	5.0	3.0	0.27	0.24	0.34	0.60	0.31	0.42
6288-H	5.0	4.0	0.28	0.63	0.34	0.65	0.31	0.64

Absolute control cultures

TREATMENT		CULTURE 1		CULTURE 2		CULTURE 3		AVERAGE
Fe (p.p.m.)	Mn (p.p.m.)	Pot 1	Pot 2	Pot 1	Pot 2	Pot 1	Pot 2	
4.0	0.5	0.63	0.53	0.61	0.65	0.63	0.56	0.60
0	0.5	0.41	0.44	0.45	0.55	0.48	0.54	0.48

The amounts of manganese absorbed by the plants grown in the frit cultures of the iron series 6285 and 6286 were of the same order of magnitude as in their corresponding control plants in most cases. The higher concentrations of manganese detected in the corresponding control plants were largely compensated by their smaller total weight

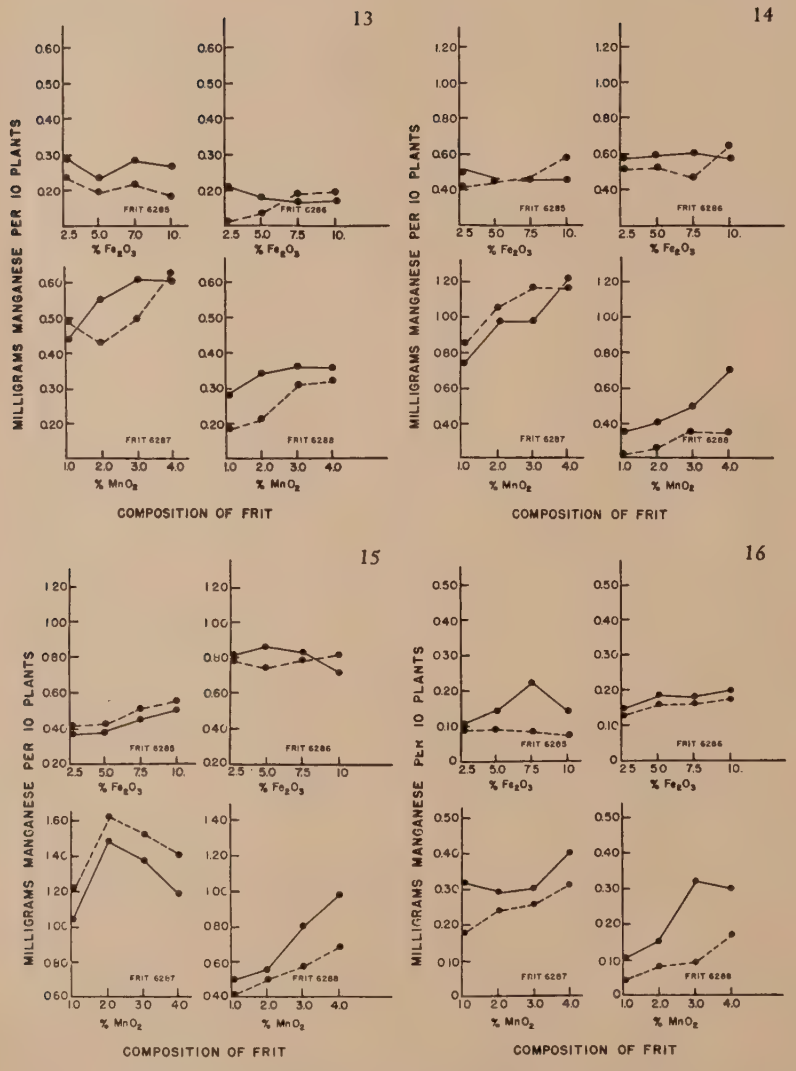

FIG. 13. Milligrams of manganese absorbed per ten plants grown in frits and their corresponding control cultures. Nutrient solutions pH = 4.0.

FIG. 14. Milligrams of manganese absorbed per ten plants grown in frits and their corresponding control cultures. Nutrient solutions pH = 5.0.

FIG. 15. Milligrams of manganese absorbed per ten plants grown in frits and their corresponding control cultures. Nutrient solutions pH = 6.0.

FIG. 16. Milligrams of manganese absorbed per ten plants grown in frits and their corresponding control cultures. Nutrient solutions pH = 7.0.

of dry matter. There were no indications that the amount of iron present in the frit exerted an influence on the amount of manganese absorbed.

The total amounts of manganese absorbed by the plants grown in the manganese-containing frits in most cases increased as the amount

TABLE 41. *Total manganese absorbed, expressed as milligrams per ten plants, grown in the frits, their corresponding quartz control cultures, and the absolute control cultures supplied with nutrient solution at pH = 6.0.*

FRIT			MILLIGRAMS MANGANESE ABSORBED PER 10 PLANTS					
No.	Composition (percent)		Culture 1		Culture 2		Average	
	Fe_2O_3	MnO_2	Quartz	Frit	Quartz	Frit	Quartz	Frit
6285-A	2.5	0	0.45	0.39	0.43	0.43	0.44	0.41
6285-B	5.0	0	0.44	0.35	0.42	0.41	0.43	0.38
6285-C	7.5	0	0.54	0.47	0.43	0.44	0.49	0.46
6285-D	10.0	0	0.45	0.39	0.55	0.53	0.50	0.46
6287-A	5.0	1.0	0.72	0.64	1.11	1.00	0.92	0.82
6287-B	5.0	2.0	1.13	1.22	1.66	1.38	1.40	1.30
6287-C	5.0	3.0	1.06	1.20	1.32	0.99	1.19	1.10
6287-D	5.0	4.0	0.97	0.90	1.25	0.90	1.11	0.90
6286-E	2.5	0	0.55	0.57	0.55	0.55	0.55	0.56
6286-F	5.0	0	0.43	0.68	0.56	0.52	0.50	0.60
6286-G	7.5	0	0.47	0.60	0.57	0.44	0.52	0.52
6286-H	10.0	0	0.30	0.35	0.59	0.54	0.45	0.45
6288-E	5.0	1.0	0.31	0.53	0.41	0.44	0.36	0.49
6288-F	5.0	2.0	0.48	0.53	....	....	0.48	0.53
6288-G	5.0	3.0	0.64	0.71	0.64	0.99	0.64	0.85
6288-H	5.0	4.0	0.74	0.75	0.72	1.03	0.73	0.89

Absolute control cultures

TREATMENT		CULTURE 1		CULTURE 2		CULTURE 3		AVERAGE
Fe (p.p.m.)	Mn (p.p.m.)	Pot 1	Pot 2	Pot 1	Pot 2	Pot 1	Pot 2	
4.0	0.5	0.38	0.44	0.37	0.46	0.41	0.45	0.42
0	0.5	0.67	0.59	0.42	0.48	0.65	0.56	0.56

of manganese in the frit was increased. The same relationship held true for their corresponding control plants.

The most manganese was absorbed by the plants grown in the 6287 frit series. The control plants corresponding to this frit series usually absorbed more manganese than those grown in the 6288 frit series.

3. Summary

A review of the data pertaining to the absorption of manganese by the plants suggest the following conclusions:

1. The concentrations of manganese in the dry matter of the corresponding control plants is of the same order of magnitude as in the frit-grown plants when the data from the cultures maintained

TABLE 42. *Total manganese absorbed, expressed as milligrams per ten plants, grown in the frits, their corresponding quartz control cultures, and the absolute control cultures supplied with nutrient solution at pH = 7.0.*

FRIT			MILLIGRAMS MANGANESE ABSORBED PER 10 PLANTS					
No.	Composition (percent)		Culture 1		Culture 2		Average	
	Fe_2O_3	MnO_2	Quartz	Frit	Quartz	Frit	Quartz	Frit
6285-A	2.5	0	0.10	0.07	0.11	0.15	0.11	0.11
6285-B	5.0	0	0.10	0.12	0.08	0.16	0.09	0.14
6285-C	7.5	0	0.05	0.23	0.11	0.18	0.08	0.21
6285-D	10.0	0	0.04	0.08	0.09	0.15	0.07	0.12
6287-A	5.0	1.0	0.20	0.27	0.14	0.36	0.17	0.32
6287-B	5.0	2.0	0.30	0.31	0.16	0.30	0.23	0.31
6287-C	5.0	3.0	0.30	0.26	0.18	0.35	0.24	0.30
6287-D	5.0	4.0	0.34	0.39	0.23	0.36	0.29	0.38
6286-E	2.5	0	0.14	0.16	0.14	0.14	0.14	0.15
6286-F	5.0	0	0.16	0.15	0.17	0.21	0.17	0.18
6286-G	7.5	0	0.15	0.14	0.14	0.18	0.15	0.16
6286-H	10.0	0	0.14	0.13	0.16	0.20	0.15	0.17
6288-E	5.0	1.0	0.06	0.14	0.03	0.05	0.05	0.10
6288-F	5.0	2.0	0.11	0.16	0.05	0.12	0.08	0.14
6288-G	5.0	3.0	0.14	0.22	0.08	0.40	0.11	0.31
6288-H	5.0	4.0	0.14	0.29	0.18	0.26	0.16	0.28

Absolute control cultures

TREATMENT		CULTURE 1		CULTURE 2		CULTURE 3		AVERAGE
Fe (p.p.m.)	Mn (p.p.m.)	Pot 1	Pot 2	Pot 1	Pot 2	Pot 1	Pot 2	
4.0	0.5	0.13	0.14	0.15	0.12	0.32	0.23	0.18
0	0.5	0.18	0.19	0.15	0.15	0.15	0.14	0.16

at pH = 4.0 is considered. In the other experiments, the corresponding control plants of the frit series 6285, 6286 and 6287 contained significantly more manganese than did the frit-grown plants. The corresponding control plants of the frit series 6288 contained about the same amount of manganese as the frit-grown plants. The data

indicate that the corresponding control plants of the manganese-containing series of frits had access to appreciable amounts of manganese, which show that the manganese in the frits was relatively soluble.

2. There was a strongly positive relationship between the total amounts of manganese absorbed by the plants and the amounts in the frits. This relationship existed both for the frit-grown plants and for their corresponding control plants which indicated that the amounts of manganese dissolved from the frits by the nutrient solution increased as the amounts of manganese in the frits increased.

TABLE 43. *Milligrams of iron per carboy of nutrient solution at the end of the experimental period maintained at pH = 4.0.*

FRIT	CARBOY		AVERAGE
	1	2	
6285-A	3.4	4.4	3.9
6285-B	5.7	4.2	5.0
6285-C	4.7	3.8	4.3
6285-D	5.6	3.1	4.4
6286-E	3.8	6.3	5.1
6286-F	5.7	7.8	6.8
6286-G	3.4	3.6	3.5
6286-H	8.4	3.6	6.0

Absolute control cultures

TREATMENT	CARBOY				AVERAGE
	1	2	3	4	
Fe added.....	25.0	18.8	36.0	20.2	25.0
Fe not added...	4.2	3.3	4.2	2.7	3.6

3. The large amounts of manganese absorbed by the plants grown in the 6287 series as compared to the plants grown in the 6288 series indicated that the manganese in the 6287 frits was more available to the plants than that in the 6288 frits. The large amounts of manganese absorbed by the control plants corresponding to the frit series 6287 as compared to the amounts absorbed by the control plants corresponding to the 6288 series, likewise indicate a greater solubility of the manganese in the 6287 frits than in the 6288 frits.

IV. DISCUSSION

The most striking results of the experiments were the differences in growth between the plants grown in the frit cultures and in their

corresponding control cultures. The frit-grown plants generally were larger and exhibited a greener and healthier appearance. The better growth of these plants grown in contact with the iron-containing frits must have been due to contact absorption of iron from the frit.

The objection may be put forth that the iron in the frit may have been soluble but did not reach the plant roots in the control culture due to precipitation in the carboy containing the nutrient solution. In order to test this possibility, the iron in the solutions were determined at the end of the experimental periods. The results are presented in tables 43 and 44. It was found that negligible amounts of iron were present in the solutions, and that these amounts were of the same

TABLE 44. *Milligrams of iron per carboy of nutrient solution at the end of the experimental period maintained at pH = 7.0.*

FRIT	CARBOY		AVERAGE
	1	2	
6285-A	3.8	14.0	8.9
6285-B	7.0	11.5	9.3
6285-C	7.7	10.2	9.0
6285-D	7.7	10.2	9.0
6286-E	7.0	7.0	7.0
6286-F	8.3	6.4	7.4
6286-G	8.3	4.5	7.4
6286-H	8.9	2.6	5.8

Absolute control cultures

TREATMENT	CARBOY			AVERAGE
	1	2	3	
Fe added	56.3	....	....	56.3
Fe not added	7.7	7.6	5.1	6.8

order of magnitude as those in the *absolute* control solutions receiving no iron. The concentrations detected in other experiments were of the same low magnitude.

However, figure 12 shows that the control plants corresponding to the 6285 frit series made a better growth and absorbed slightly more iron than did the control plants corresponding to the 6286 frit series. The explanation for this difference seemed to be that the control plants corresponding to the 6285 frit series had a slightly better access to iron than the control plants corresponding to the 6286 frit series. In spite of the negligible amounts of iron found in the nutrient solutions, it was not possible to rule out completely the possibility that a small

amount may have been released by the nutrient solution flooding the 6285 frits. However, the amounts released were not sufficient to prevent the appearance of chlorosis and stunted growth of the plants.

Another fact pointing towards a slight solubility of the iron in the frits was the close parallelism observed between iron absorption by the frit-grown plants and by their corresponding control plants. This parallelism is clearly demonstrated by the curves indicating the parts per million of iron in the dry matter of the plants grown in the 6285 frit series and in their corresponding control plants, and also in the plants grown in the 6286 frit series and their corresponding control cultures.

TABLE 45. *Ratio of iron to manganese in the dry material grown in the frits and their corresponding control cultures supplied with nutrient solution at pH = 5.5.*

FRIT			IRON : MANGANESE RATIO					
No.	Composition (percent)		Culture 1		Culture 2		Average	
	Fe_2O_3	MnO_2	Quartz	Frit	Quartz	Frit	Quartz	Frit
6285-A	2.5	0	0.23	0.58	0.44	0.59	0.34	0.59
6285-B	5.0	0	0.25	0.47	0.37	0.60	0.31	0.54
6285-C	7.5	0	0.38	0.55	0.30	0.82	0.34	0.69
6285-D	10.0	0	0.30	0.62	0.26	0.61	0.28	0.62
6287-A	5.0	1.0	0.16	0.76	0.24	0.39	0.20	0.58
6287-B	5.0	2.0	0.30	0.38	0.30	0.54	0.30	0.46
6287-C	5.0	3.0	0.17	0.42	0.25	0.50	0.21	0.46
6287-D	5.0	4.0	0.15	0.29	0.31	0.48	0.23	0.39
6286-E	2.5	0	0.15	0.25	0.28	0.39	0.22	0.32
6286-F	5.0	0	0.20	0.36	0.21	0.29	0.21	0.33
6286-G	7.5	0	0.17	0.31	0.26	0.38	0.22	0.35
6286-H	10.0	0	0.30	0.43	0.19	0.34	0.25	0.39
6288-E	5.0	1.0	0.70	0.66	0.91	1.02	0.81	0.84
6288-F	5.0	2.0	0.53	0.49	0.90	0.77	0.72	0.63
6288-G	5.0	3.0	0.38	0.79	0.61	0.61	0.50	0.70
6288-H	5.0	4.0	0.41	0.39	0.37	0.45	0.39	0.42

In contrast to the great insolubility of the iron in the frits, the manganese exhibited a considerable solubility as indicated by the amounts absorbed by the corresponding control plants, A relatively large solubility of the manganese was evidenced further by chemical analyses of the nutrient solutions flooding the manganese-containing frits. Figure 17 indicates the amounts dissolved by the various nutrient solutions. The largest amounts were dissolved from the 6287 frits and the pH value of the nutrient solution had a conspicuous influence. At pH = 4.0, the nutrient solution dissolved about twice as much manganese as at pH = 7.0.

Owing to the comparatively high solubility of the manganese in the frits, there was no basis to judge the extent to which the plant roots were able to absorb manganese by contact with the frit particles. The better growth of the plants grown in the manganese frits as compared to their corresponding control cultures must be ascribed to an effect of the iron in the frits.

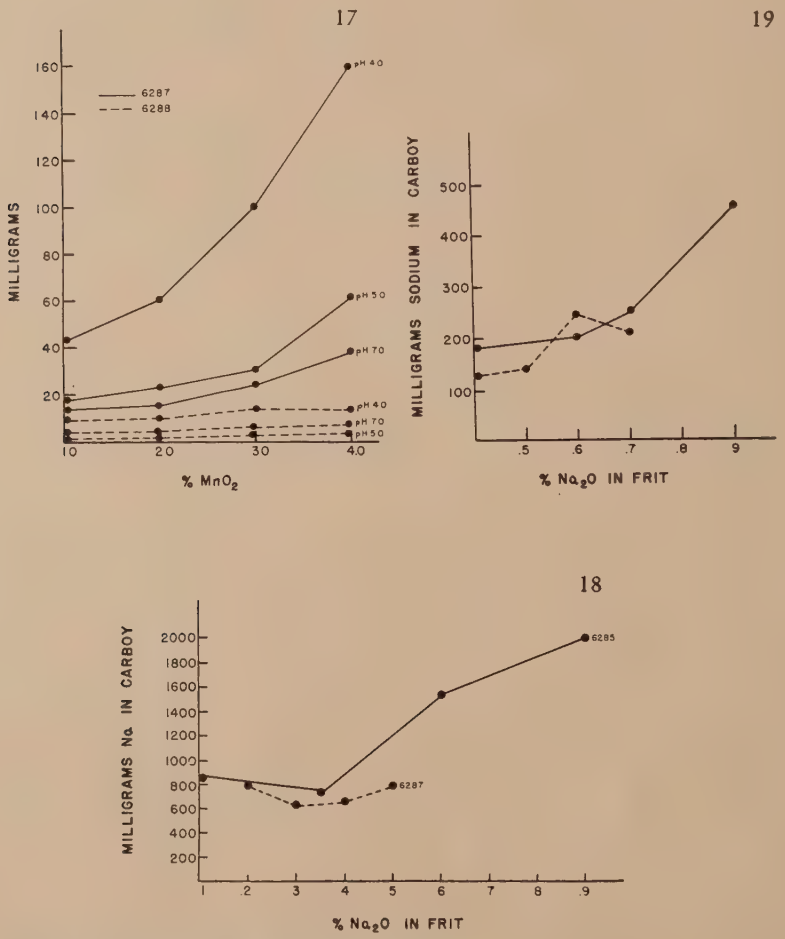

FIG. 17. Milligrams of manganese accumulated in the carboy of nutrient solution at the end of the growing period. Frit 6287, solid lines; frit 6288, broken lines.

FIG. 18. Milligrams of sodium accumulated in the carboy of nutrient solution at the end of the growing period. Nutrient solution ph = 4.0. Frit 6285, solid line; frit 6287, broken line.

FIG. 19. Milligrams of sodium accumulated in the carboy at the end of the growing period. Nutrient solution pH = 4.0. Frit 6286, solid line; frit 6288, broken line.

It is evident from many reports in the literature than iron and manganese are interrelated functionally in their physiological effect on plants. Tottingham and Beck (1916) reported that the best growth was obtained when the ratio of iron to manganese in the nutrient solution was 1:1.

More recently Somers and Shive (1942) reported that the best growth of soybeans in solution culture was obtained when the ratio of iron to manganese was close to 2.5 : 1, the absolute concentration of the elements being of lesser importance than the ratio of their concentrations. The ratio of iron to manganese in the nutrient solution flooding the manganese-containing frits used in the present experiments was extremely low, especially in the case of the 6287 frit series. It is apparent from figure 17 that at pH = 4.0, the frit 6287-D containing 4.0 percent manganese dioxide released 10 parts per million of manganese to the solution by the end of the experimental period. Table 43 shows that the iron concentration of the solution was about 5 milligrams per carboy or 0.3 part per million which gave a ratio of iron to manganese of about 0.03:1, a value far below the optimum reported in literature. The possibility exists, therefore, that the chlorotic condition and stunted growth observed in the corresponding control cultures was due to manganese toxicity. If this is true, it is of interest to note that the plants grown in the frit cultures did not show toxicity symptoms although they were supplied with the same high concentrations of manganese as were their corresponding control plants. The effect of root contact with the frits must have eliminated the unfavorable iron-manganese ratio by permitting the absorption of additional iron from the frit.

Assuming that the concentrations of iron and manganese in the plant material was determined largely by their concentrations in the media, the ratio of iron to manganese in the dry matter of the plants should give an indication of the relative availability of these ions to the plant roots. This ratio was calculated for the plant materials obtained in the experiment carried out at pH = 5.0. The data presented in table 45 show that the ratio of iron to manganese in the corresponding control plants was smaller than in the frit-grown plants. This situation indicates that the frit-grown plants actually did have a better access to iron than their corresponding control plants. It is interesting to note that the difference in the iron-manganese ratio in the corresponding control plants and the frit-grown plants was larger in the case of the 6285 and 6287 frit series than in the 6286 and 6288 frit series. This is an indication that the plants grown in the frits of the 6285 and 6287 series absorbed relatively more iron than those grown in the 6286 and 6288 frits.

The difference in the growth and composition of the plants grown in frits of the 6285 and 6287 series when compared to the effects of of the frits of the 6286 and 6288 series were very pronounced. In fact, the difference between the influence of the different series of frits was greater than the effect of changes in the iron and manganese concentration of the individual frits within the series. The chief difference between the two classes of frits is that the 6286 and 6288 frits contained about 40 percent more silica than the 6285 and 6287 frits. This differ-

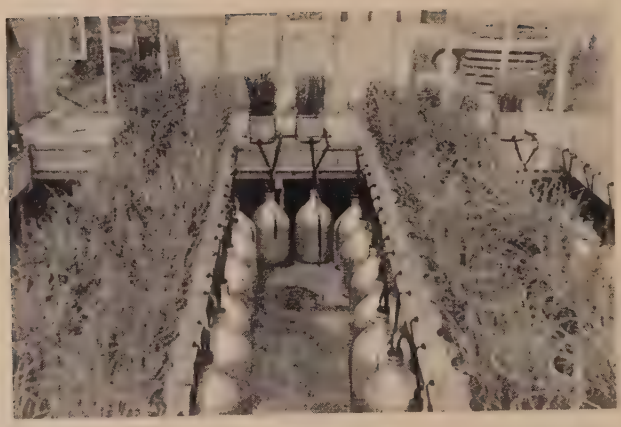

FIG. 20. Arrangement of the culture pots used in the study of glass frits.

FIG. 21. Arrangement of the pairs of culture pots. The pot on the left side of each pair contains the experimental frit, and the one on the right contains quartz gravel. The greater size and darker color of the plants growing in the frit are clearly evident. The culture solution in the carboy was forced upward into the culture pots by air pressure every four hours; therefore components dissolved from the frit became equally available to both cultures. Components available to the plants by contact with their roots were available only to the plants growing in the frit.

ence in the basic formula of the matrix markedly influenced the solubility as indicated by the data for manganese release presented in figure 17.

Figures 18 and 19 indicate the amounts of sodium dissolved from the frits by the nutrient solution maintained at a pH = 4.0. Again, larger amounts of this substance were released from the 6285 and 6287 frits than from the 6286 and 6288 frits. The correlation between

FIG. 22. A typical pair of experimental cultures showing the availability of iron in glass frit to wheat plants. The culture pot on the left contained frit A-6285-A. This frit contained 2.5 percent Fe_2O_3. Nutrient solution from a single carboy flooded both pots every four hours. The obvious superiority of the wheat plants growing in the frit shows that iron was released to them by root contact. The corresponding control plants growing in the quartz filled pot on the right show acute symptoms of iron deficiency even though their roots are flooded every four hours with the nutrient solution leachate from the frit culture.

the amounts of sodium presented in the frits and the amounts dissolved by the nutrient solution was apparent. Similar tests were made for the accumulation of potassium and phosphorus in the nutrient solutions, but since these ions were added to the nutrient solution in comparatively large amounts, it was difficult to detect the small amounts which might have been derived from the frits.

FIG. 23. A typical pair of experimental cultures showing the availability of both iron and manganese in glass frit to wheat plants. The culture pot on the left contained frit A-6287-A. This frit contained 5.0 percent of Fe_2O_3 and 1.0 percent of MnO_2. The pot on the right contained quartz gravel. Both pots were flooded every four hours with nutrient solution from the same carboy. The solution was complete except that iron and manganese were lacking. The larger size and darker color of the plants growing in the frit show that iron and manganese were released.

FIG. 24. Another pair of experimental culture pots showing the superiority of the wheat plants grown in frit A-6287-A. This frit contained 5.0 percent of Fe_2O_3 and 1.0 percent of MnO_2. The pot on the left contained quartz gravel. Both pots were flooded every four hours with nutrient solution from a common carboy. The solution was complete except that iron and manganese were lacking.

FIG. 25. A general view of the experimental wheat plants just before harvesting. The frit-filled pot of each connected pair of pots bears the identification number of the frit. The pair of pots on the extreme left are the control cultures which received neither iron nor manganese. The plants growing in these cultures were acutely cholorotic and only about half as tall as those growing in the experimental frits. All cultures received identical nutrient solutions. These solutions were complete except that iron and manganese were lacking.

A general conclusion which could be drawn from the present investigation was that glass frits can be developed in which plant nutrients are held with forces strong enough to prevent their dissolution in water but which do not prevent them from being dissolved by acid solutions or from being absorbed by root surfaces. Since the relative differences in the growth of the plants grown in frit and in their corresponding control cultures were larger at pH = 7.0 than at pH = 4.0, one might assume that a contact absorption was relatively more prominent at high than at the low pH values.

The possible use of frit as a source of minor elements in large scale hydroponic gravel cultures is apparent. One of the main difficulties encountered in this type of crop production is the maintenance of a sufficient supply of iron for normal plant growth. Frequent adjustments of the pH value is necessary in order to maintain a proper iron concentration in the solution flooding the plant roots. The results of the present experiments indicate that wheat plants can grow normally without developing chlorosis at a pH value of 7.0 if the roots are in contact with iron-containing frit.

While the development of frits with the property of releasing iron and manganese to plant roots has been based mainly upon greenhouse studies, a few experiments have been carried out in soil under field conditions. Wynd and Stromme (1951) applied a finely ground manganese-containing frit to a calcareous soil and obtained an increased yield and manganese content of the seeds and stems of bean plants. The iron content was appreciably decreased. These results suggested that the ratios of iron to manganese in the frit must be carefully adjusted in order to aviod unfavorable ratios of available iron to manganese in the soil. Wynd and Bowden (1951 a) applied a finely ground iron-containing frit to a fertile greenhouse soil and obtained increased growth of snapdragons, which indicated that iron may be a limiting factor for plant growth even though no visible deficiency symptoms are visible. These investigators (1951 b) also were able to eliminate chlorosis of blueberries by adding an iron-containing frit to the soil.

Due to the complexity of the factors responsible for minor element deficiencies in plants, the development of frits with the property of eliminating specific deficiencies when applied to the soil can only be obtained through further studies.

V. Summary and Conclusions

1. The use of especially compounded glass frits as sources of iron and manganese for plants was suggested. Successful preliminary experiments were carried out to explore the value of such frits as sources of iron to plants.

2. Two frits, one containing 40 percent SiO_2 and 21 percent of P_2O_5 and one containing 59 percent of SiO_2 and 15 percent of P_2O_5, gave good results in preliminary experiments and were used for the present study. Two series of each type of frit were prepared; one series contained 2.5, 5.0, 7.5, and 10.0 percent of Fe_2O_3 and no manganese, and the other contained 1.0, 2.0, 3.0, and 4.0 percent of MnO_2, all containing 5.0 percent Fe_2O_3. The chemical compositions of the 16 exprimental frits were given.

3. The experiments were carried out by using the frit as a supporting medium in hydroponic gravel culture. The growth and chemical composition of wheat plants grown in each frit were compared with the results obtained from plants grown in quartz gravel. Both pots were flooded at four-hour intervals with identical nutrient solution supplied from the same carboy. The nutrient solution was complete except that iron was omitted when iron was the variable factor in the frit, and both iron and manganese were omitted when these nutrients were the variable factors in the frit. A uniform pH value was maintained in the nutrient solutions. Experiments were carried out at pH values of 4.0, 5.0, 6.0, and 7.0.

4. Descriptions of the visual appearance of the plants together with tables and graphs were presented showing the fresh and dry weights of the plants and their absorptions of iron and manganese.

5. The frit cultures produced normally green plants over the entire range of pH values of the nutrient solutions. The corresponding quartz control cultures produced more or less chlorotic plants whose growth, as judged by fresh and dry weight data, was inferior to that produced by the frit cultures. The series of frit containing the lowest silica content produced significantly larger plants at all pH levels than nutrient solution containing 4.0 parts per million of iron and 0.5 parts per million of manganese.

6. The data for the fresh and dry weights and for the absorption of iron by the plants, together with data showing the insolubility of the iron in the frits indicated that the plants were able to obtain iron from the frits by contact absorptions. Data for manganese absorption and manganese accumulation in the nutrient solution indicated a relatively large solubility of manganese, especially at low pH values. Consequently no conclusion could be drawn concerning the extent of contact absorption of the manganese in the frit.

VI. LITERATURE CITED

Alberts, W. B. 1934. Further observations on manganese deficiency in oats at Florence, South Carolina. South Carolina Agr. Exp. Sta., 47th Ann. Rep. p. 45.

Badger, A. E., and **R. H. Bray.** 1945. Soluble glass may offer fertilizer possibilities. Chem. and Met. Eng. **52** (4): 112–113.

Bennett, J. P. 1927. The treatment of lime-induced chlorosis in fruit trees. Phytopathology **17**: 745–746.

Chandler, W. V., and **G. D. Scarseth.** 1941. Iron starvation as affected by overphosphating and sulfur treatment on Houston and Sumter Clay soils. J. Am. Soc. Agron. **33**: 93–104.

Chapman, H. D. 1939. Absorption of iron from finely ground magnetite by Citrus seedlings. Soil Sci. **48**: 309–317.

Conner, S. D. 1932. Factors affecting manganese availability in soils. J. Am. Soc. Agron. **24**: 726–733.

Eaton, F. M. 1936. Automatically operated soil-culture equipment. Jour. Agr. Res. **53**: 433–444.

Gilbert, B. E. 1934. Normal crops and the supply of available soil manganese. Rhode Island Agr. Exp. Sta., Bul. **246.**

———, **F. T. McLean** and **L. J. Hardin.** 1926. The relation of manganese and iron to a lime-induced chlorosis. Soil Sci. **22**: 437–446.

Guest, P. L. 1944. Root contact phenomena in relation to iron nutrition and growth of Citrus. Proc. Am. Soc. Hort. Sci. **44**: 43–48.

Hummell, F. G., and **H. H. Willard.** 1938. Determination of iron in biological materials. Ind. Eng. Chem., Anal. Ed. **10**: 13–15.

Inskeep, G. C. 1951. Frit for flowers. Ind. Eng. Chem. **43** (3): p. 17A.
Jenny, H., and **R. Overstreet.** 1938. Contact effects between plant roots and soil colloids. Proc. Nat. Acad. Sci. U. S. **24:** 384–392.
Johnson, M. O. 1917. Manganese as a cause of the depression of the assimilation of iron by pineapple plants. J. Ind. Eng. Chem. **9:** 47–49.
Lindner, R. C., and **C. P. Harley.** 1944. Nutrient interrelations in lime-induced chlorosis. Plant Physiol. **19:** 420–439.
McGeorge, W. T. 1923. The chlorosis of pineapple plants grown on manganiferous soils. Soil Sci. **16:** 269–274.
Olsen, C. 1935. Iron absorption and chlorosis in green plants. Compt. rend. trav. lab. Carlsberg. Ser. Chim. **21:** 15–52. (Abs. in Chem. Abs. **29:** 7398. 1936.)
Rippel, A. 1923. Über die durch Mangan verursachte Eisenchlorose bei grünen Pflanzen. Biochem. Z. **140:** 315–323.
Samuel, G., and **C. S. Piper.** 1928. Grey Speck (Manganese deficiency) disease of oats. J. Dept. Agr. S. Australia **31:** 696–705, 789–799.
Schreiner, O., and **P. R. Dawson.** 1927. Manganese deficiency in soils and fertilizers. Ind. Eng. Chem. **19:** 400–404.
Sherman, G. D., and **P. M. Harmer.** 1941. Manganese deficiency of oats on alkaline organic soils. J. Am. Soc. Agron. **33:** 1080–1092.
Shive, J. W. 1915. A three-salt solution for plants. Am. J. Botany **2:** 127–160.
Sideris, C. P., and **B. H. Kraus.** 1933. The effect of sulphur and phosphorus on the availability of iron to pineapple and maize plants. Soil Sci. **37:** 85–97.
Skinner, J. J., and **R. W. Ruprecht.** 1930. Fertilizer experiments with truck crops. III. Truck crops with manganese on calcareous soil. Florida Agr. Exp. Sta. Bul. **218:** pp. 37–65.
Somers, I. I., and **J. W. Shive.** 1942. The iron-manganese relation in plant metabolism. Plant Physiol. **17:** 582–603.
Thorne, D. W., and **A. Wallace.** 1944. Some factors affecting chlorosis of high lime soils. I. Ferrous and Ferric iron. Soil Sci. **57:** 299–311.
Tottingham, W. E., and **A. J. Beck.** 1916. Antagonism between manganese and iron in the growth of wheat. Plant World **19:** 359–470.
Wain, R. L., B. J. Silk, and **C. B. Wills.** 1943. The fate of manganese sulfate in alkaline soils. J. Agr. Sci. **33:** 18–22.
Wallace, T. 1928. Investigations on chlorosis of fruit trees. II. The composition of leaves, bark, and wood of current season's shoots in cases of lime-induced chlorosis. J. Pomol. Hort. Sci. **7:** 172–183.
Wallace, T. 1939. Investigations on chlorosis of fruit trees. IV. The control of lime-induced chlorosis in the field. J. Pomol. Hort. Sci. **7:** 251–269.
———, and **L. Ogilvie.** 1941. Manganese deficiency of Agricultural and Horticultural crops. Summary of investigations, season 1941. Ann. Rep. Agr. and Hort. Research Sta., Long Ashton, Bristol, 1941, pp. 45–48.
———, and **E. J. Hewitt.** 1946. Studies in iron deficiency of crops. I. Problems of iron deficiency and the interrelationships of mineral elements in iron nutrition. J. Pomol. Hort. Sci. **22:** 153–161.
Willard, H. H., and **L. H. Greathouse.** 1917. The colorimetric determination of manganese by oxidation with periodate. J. Am. Chem. Soc. **39:** 2366–2377.
Willis, L. G. 1928. Response of oats and soybeans to manganese on some coastal plain soils. North Carolina Agr. Exp. Sta. Bul. **257.**
———. 1932. The effect of liming soils on the availability of manganese and iron. J. Am. Soc. Agron. **24:** 716–726.
Wynd, F. L. 1950. The use of iron containing frits as a new medium for hydroponic culture. Michigan Agr. Exp. Sta., Quart Bul. **33,** pp. 52–53.
———. 1951. Availability to wheat plants of iron in very insoluble glassy frits. Lloydia **14:** 1–33.
———, and **R. A. Bowden.** 1951 a. Response of snapdragons to very insoluble iron-containing frit. Lloydia **14:** 34–39.
———, ———. 1951 b. Response of chlorotic blueberry bushes to a very insoluble iron-containing glassy frit. Lloydia **14:** 55–57.
Wynd, F. L., and **E. R. Stromme.** 1951. Absorption of manganese and iron by Navy bean plants grown in a calcareous soil fertilized with a manganese-containing glassy frit. Lloydia **14:** 40–54.
Zimmerley, H. H. 1926. Soil acidity in relation to spinach production. Virginia Truck Sta., Bul. **57.** (Abs. in Exp. Sta. Rec.)

Glass Frit as a Source of Iron and Manganese for Roses Grown in Hydroponic Culture[1]

F. Lyle Wynd[2]

Table of Contents

I. Introduction

One of the problems encountered in the hydroponic culture of roses is the difficulty of maintaining the proper concentrations of iron and manganese in the nutrient solution. Superficially, this difficulty may appear to be one easily avoided by adding the correct amounts of these nutrient in soluble form. However, it is exceedingly difficult to maintain the proper concentrations of these ions in a large volume of nutrient solution stored in a tank and pumped periodically through the gravel substratum in the culture bench. Unavoidable changes in the pH value of the solution and even variations in the temperature of different areas in the greenhouse, seriously influence the ability of the plants to absorb adequate amounts of these troublesome nutrients. Some growers have informed the author that they have experienced little or no difficulty in this respect, but others have abandoned the commercial hydroponic culture of roses because they found it impossible to maintain the proper concentrations of the necessary trace nutrients in the nutrient solution, or at least they found it so difficult as to make the procedure commercially impractical.

The problem of controlling the trace nutrients in the culture solution would be solved if the gravel in the culture bench could be replaced by material so fabricated that it would itself supply the plants with these nutrients through contact with the roots of the growing plants. Such a material not only should release adequate amounts of iron and manganese to the plants, but in addition should exert no significant effect on the pH value of the nutrient solution.

Wynd (1950) reported briefly the use of very insoluble glass frit as a source of iron to several species of agriculturally important plants. Later, Wynd (1951) published a detailed report of the availability of iron in these frits to wheat plants grown in hydroponic cultures.

[1]The expenses of this investigation were borne by a grant-in-aid provided by the Ferro Corporation, Cleveland, Ohio.

[2]Research Professor, Department of Botany and Plant Pathology, Michigan State College, East Lansing, Michigan.

Wynd and Bowden (1951a, 1951b) extended the study to include snapdragons grown in greenhouse soil under commercial conditions and to blueberries grown in an iron-deficient clay soil in the field. Wynd and Stromme (1951) described the availability of manganese in a glass frit to white beans grown under commercial conditions in a manganese-deficient calcareous soil. Stromme and Wynd (1953) later reported the results of a detailed study of the effect of the pH value of the hydroponic culture solutions on the absorption of iron and manganese by wheat.

The above studies showed the general effectiveness of very insoluble glass frit as a source of iron and manganese to plants. They also presented evidence that the iron in the frit was available to the plants by contact exchange with the roots, even though the frit was insoluble in water as defined by ordinary standards. Manganese in the frit, on the other hand, was comparatively soluble, and this solubility was found to be influenced by the pH value of the nutrient solutions in contact with it. Therefore, the pH value of the solution was shown to be an important factor if both iron and manganese were supplied to the plants by the same frit. This appears to be all the more necessary when the extensive published data concerning the importance of the iron-manganese ratio in plants is recalled.

The successful use of glass frit as a source of iron and manganese to several kinds of plants under various cultural conditions suggested the present study of its use for the hydroponic culture of roses.

II. Experimental Methods and Materials

The mechanical details of the experimental hyroponic cultures used in the present investigation were similar to those described by Wynd (1951). The culture pots were 2-gallon, glazed earthenware. They were so arranged that two pots were connected to each reservoir of nutrient solution. One member of each pair contained the glass frit, while the other contained quartz gravel. The five-gallon carboys serving as the reservoirs of nutrient solution were placed beneath the greenhouse bench and every four hours an electric time-clock activated a motor-driven air pump which forced air into them from a common pressure line, thus causing the nutrient solution to flood simultaneously the pair of culture pots connected to each carboy. After seven minutes, the air compressor automatically stopped thereby permitting the solutions to drain back into their respective reservoirs. Any soluble components in the frits therefore would accumulate in the reservoir of nutrient solution supplying the connected pair of cultures and would become equally available to both. One of these cultures comprising the connected pair was the frit culture and the other was its *corresponding* control culture. Components of the frit supplied to the plants by direct contact with roots would be available only to the plants grown in the frit culture.

Since the investigation was concerned with the availability of iron and manganese in the frit, these nutrients were omitted from the culture solutions. The solutions contained all other necessary nutrients.

A three-salt nutrient solution proposed by Shive (1915), but only half as concentrated, was used as the culture medium, the composition of which was as follows:

Salt	Grams per Liter
$MgSO_4 \cdot 7H_2O$	1.85
$Ca(NO_3)_2 \cdot 4H_2O$	0.61
KH_2PO_4	1.23

Although Shive originally proposed this nutrient solution for the culture of wheat in hydroponic cultures, it has been found that it supports excellent growth of many kinds of plants. It was used for the present study because of its simplicity and the ease with which it could be prepared. Specialists in the commerical hydroponic production of roses doubtlessly would prefer to use a nutrient solution more specifically adapted for the culture of this crop.

The nutrient solutions also contained the following concentrations of the trace nutrients.

Form Added	Nutrient	Parts per Million
HBO_3	Boron	0.50
MO_3	Molybdenum	0.05
$CuSO_4 \cdot 5H_2O$	Copper	0.02
$ZnSO_4 \cdot 7H_2O$	Zinc	0.05

Twenty-four carboys, each supplying a pair of culture pots as described above, were used in the experiment. The influence of the pH value of the solution on the release of iron and manganese to the plants from the frit was studied by maintaining quadruplicate carboys of nutrient solution at pH = 4.0, 5.5, and 7.0.

Absolute control cultures were arranged by growing plants in quartz gravel of the same particle size as the frit, and supplied with the nutrient solution described above but which contained four parts per million of iron and 0.5 part million of manganese. The plants produced by these cultures were designated as the *absolute* controls in contrast to the *corresponding* controls grown in the quartz-filled pot in conjuction with each frit-filled pot.

The glass frit was prepared by Charles A. Vana of the Ferro Corporation, Cleveland, Ohio, and is identified in its records as A-6300-B. It contained 7.5 per cent iron in terms of Fe_2O_3 and 3.0 per cent manganese in terms of MnO_2. This type of frit had produced excellent growth of wheat in previous experiments.

Young rose plants of the variety Better Times were selected for uniform size and planted in the culture pots October 4, 1950. The plants were rooted cuttings grown in 3-inch pots. The soil was carefully washed from the roots before the plants were placed in the gravel cultures.

The plants remained in the experimental cultures for a period of four months. The nutrient solutions were renewed once during that period; the *absolute* control cultures, on the other hand, received iron and manganese at weekly intervals. The original volumes of the nutrient solutions in the carboys were maintained by the addition of distilled water at weekly intervals.

III. EXPERIMENTAL RESULTS

A. VISUAL APPEARANCE OF THE PLANTS

It became apparent very early during the growth period that the rose plants growing in the frit cultures were developing more rapidly and that their leaves were exhibiting a more healthy green color than the plants growing in their *corresponding* control cultures. It should be recalled that each frit culture and its *corresponding* control were periodically flooded with nutrient solution from the same carboy. The fact that the frit-borne plants were superior in quality showed that the contact of their roots with the frit, rather than some soluble component of it, exerted a favorable effect on their growth and development.

The superiority of the frit-borne plants over their *corresponding* control plants was most evident when the nutrient solution was maintained at pH = 7.0. The difference became less obvious as the pH value decreased, until at pH = 4.0 the *corresponding* control plants were almost as good as those grown in the frit. This situation suggests that the iron in the frits became progressively more soluble and therefore available to the *corresponding* control cultures at the lower pH values of the nutrient solution.

At pH = 7.0, the plants grown in the *corresponding* control cultures soon became distinctly chlorotic, and acutely so by the end of the experimental period. The growth of these plants was so reduced that they were commercially unsatisfactory. The plants grown in the frit, however, at pH = 7.0 were normal in appearance and were of good commercial quality.

At pH = 5.5, the *corresponding* control plants also were chlorotic and smaller than those grown on the frit. However, these symptoms were less pronounced than those observed at pH = 7.0. The plants grown in the frit were normal in apperance and were of good commercial quality.

At pH = 4.0, the *corresponding* control plants were almost as satisfactory as those grown in the frit. The growth of the plants in both the frit and quartz, however, was distinctly less than in the nutrient solutions at the higher pH values. It became apparent as the experiment progressed, that pH = 4.0 was near the maximum acidity at which the rose plants could grow. This pH limitation especially was apparent from the poor growth obtained by the *absolute* control plants at this pH value even though both iron and manganese were maintained at suitable concentrations in these solutions. The roots of the *absolute* control plants grown at pH = 4.0 became brown soon after planting and the plants finally died without producing flowers. It was interesting to note that the plants in the *corresponding* control cultures fed with the same nutrient solution as the frit cultures did not show as severe injury as the *absolute* control plants grown at pH 4.0. This suggests that the iron and manganese released by the frit partially overcame the toxic effects of the comparatively high acidity of the solutions.

B. YIELD OF FLOWERS

The data assembled in Table 1 show the degree of chlorosis exhibited by the leaves and the number of flower-bearing shoots cut from the

plants grown in the frits and in their *corresponding* control cultures. When the nutrient solution was maintained at pH = 4.0. ten flowering shoots were cut from the *corresponding* control plants, three of which possessed leaves normally green in color, five of which were slightly chlorotic, and two of which were severely chlorotic. The plants grown in the frit flooded with nutrient solution at this pH value yielded 18 flowering shoots per plant, all of which possessed leaves normally green in color.

When the pH value of the nutrient solution was maintained at 5.5, 19 flowering shoots were harvested from the *corresponding* control cultures, none of which possessed normally green leaves. Three of these bore slightly chlorotic leaves and the remaining 16 bore severely chlorotic leaves. The plants grown on the frits and fed with the same

TABLE 1. *Distribution of chlorosis among flowering shoots cut from rose plants grown in frit and corresponding control cultures supplied with nutrient solutions maintained at various pH values.*

Degree of Chlorosis of Flowering Shoots	Number of Flowering Shoots Cut per Plant					
	pH = 4.0		pH = 5.5		pH = 7.0	
	Control Cultures	Frit Cultures	Control Cultures	Frit Cultures	Control Cultures	Frit Cultures
None	3	18	0	19	0	22
Slight	5	0	3	2	0	0
Severe	2	0	16	0	7	0
Total	10	18	19	21	7	22

nutrient solutions produced 21 flowering shoots. Nineteen of these possessed leaves normally green in color, and the leaves of the other two were only slightly chlorotic. None of the flowering shoots exhibited severe chlorosis.

When the pH value of the nutrient solution was 7.0 seven flowering shoots were harvested from the *corresponding* control plants. All seven bore severely chlorotic leaves. On the other hand, 22 flowering shoots were obtained from the plants grown in the frits supplied with the same nutrient solution. The leaves of none of these were chlorotic.

The data presented in table 1 and briefly described above indicate that about the same number of flowering shoots were produced by the frit cultures at all pH values of the nutrient solutions, and that the leaves on these shoots were normally green in all except two in a total of 61 shoots. On the other hand, the number of flowering shoots produced by *corresponding* control plants varied greatly with the pH value of the nutrient solution, and the leaves of these shoots were predominantly chlorotic. The influence of the pH value of the

nutrient solution on the number of commercially usable flowering shoots obtained almost disappeared when the roots of the plants were in contact with the frit.

The influence of the contact of the roots of the rose plants with the frit particles in overcoming the effect of varying pH values of the nutrient solutions is further evidenced by the data presented in table 2. These data were obtained from the *absolute* control plants grown in solutions receiving frequent additions of soluble iron and manganese, but which were maintained at different pH values. In contrast to the plants grown in contact with the frits or in solutions periodically contact with them, the *absolute* control plants produced no flowers when the nutrient solution was maintained at pH = 4.0. At pH = 5.5. eleven flowering shoots were produced, all but one of which bore normally green leaves. At pH = 7.0, 15 flowering shoots were produced, seven of which bore normally green leaves, seven slightly chlorotic leaves, and one distinctly chlorotic leaves. These data show that

TABLE 2. *Distribution of chlorosis among flowering shoots cut from rose plants grown in the absolute control cultures supplied with nutrient solution of various pH values and containing adequate iron and manganese.*

DEGREE OF CHLOROSIS OF FLOWERING SHOOTS	NUMBER OF FLOWERING SHOOTS CUT PER PLANT		
	pH = 4.0	pH = 5.5	pH = 7.0
None	0	10	7
Slight	0	1	7
Severe	0	0	1
Total	0	11	15

the best yield of commercially usable flowering shoots from the absolute control cultures was obtained at pH = 5.5. It is of especial interest to note that the number of flowering shoots produced by the *absolute* control plants, even when grown under the most favorable circumstances, was never more than about half the number produced by the frit-borne plants, irrespective of the pH values of the nutrient solutions used.

C. WEIGHT OF FLOWERS AND PLANTS

The flowering shoots described above were cut one-half inch above their third basal leaf when the flowers were fully developed. The fresh weights and lengths of all the shoots harvested during the four months of the experimental period are recorded in table 3. At all pH values of the nutrient solution, the total weights of the flowering shoots produced by the frit-borne plants were greater than those produced by their *corresponding* control plants. The greatest fresh weight yield was obtained at pH = 5.5 from both the frit cultures and their *corresponding* controls. For example, the weights produced by the frit cultures maintained at this pH value was 146 percent of that produced by the *corresponding* control cultures. The fresh weights

of the flowering shoots produced by the frit cultures at pH = 7.0 was almost as great as at pH = 5.5, although the *corresponding* control cultures produced the smallest weight of shoots observed. In this instance, the weight obtained from the frit cultures was 454 percent of that obtained from their *corresponding* control cultures. At pH = 4.0 there was distinct diminution of the total fresh weight of the flowering shoots, although the weight obtained from the frit-borne plants was 254 percent of that obtained from the *corresponding* control plants.

The data assembled in table 3 also show that the longest flowering shoots were produced when the nutrient solutions were maintained at pH = 5.5. This was true for the *corresponding* control plants as well as for those grown on the frit. At this pH value, the shoots of the *corresponding* control plants were almost as long as those of the frit-borne plants. At pH = 7.0, the length of the shoots produced by the frit cultures was almost as great as that produced at pH = 5.5, although the shoots of the *corresponding* control plants were short and unsatisfactory. At pH = 4.0, the length of the shoots of the frit-borne plants was materially lessened, and were only slightly longer than those of the *corresponding* control plants.

A survey of all the data presented in table 3 shows that the iron and manganese in the frits significantly increased the total fresh weight of flowering shoots and also increased their average weight and length in comparison with the values obtained from the plants grown in their *corresponding* control cultures. These data show clearly that the favorable effect of the frit was dependent upon the actual contact of the roots with it rather than upon its solubility. As the pH value of the nutrient solution increased, the effect of root contact with the frit became more pronounced.

The fresh weights and lengths of the flowering shoots harvested from the *absolute* control plants are assembled in table 4. It should be remembered that these plants were grown in quartz gravel periodically flooded with nutrient solution exactly like that used for the frit cultures except that it contained adequate amounts of soluble iron and manganese. Theoretically, one might assume that these plants would be the best obtainable under the experimental conditions, but the data show that this assumption is not necessarily valid.

For example, no flowers were obtained from the *absolute* control cultures when the nutrient solution was maintained at pH = 4.0 although shoots of moderate quality were produced by the frit-borne plants at this pH value. At pH = 5.5, the total weight of flowering shoots, their average fresh weight and average length were greater when the roots of the plants were in contact with the frit. At pH = 7.0. slightly superior results were obtained from the *absolute* control plants with the exception of the average length of the shoots which again was greater for those harvested from the frit-borne plants.

At the end of the experimental period, it became obvious that the plants grown as the *corresponding* controls for the individual frit cultures were so chlorotic and unhealthy in appearance that they would produce no more flowers. To have continued the experiment would have erroneously exaggerated the differences between them and the frit-borne plants, consequently the experiment was discontinued at this

TABLE 3. *Fresh weight and length of flowering shoots of roses cut from plants grown in frits and in their corresponding control cultures supplied with nutrient solutions maintained at various pH values. Average values are based on yields from six cultures.*

TYPE OF DATA	pH VALUE OF NUTRIENT SOLUTION								
	pH = 4.0			pH = 5.5			pH = 7.0		
	Control Cultures	Frit Cultures	Frit Cultures, % of Control	Control Cultures	Frit Cultures	Frit Cultures, % of Control	Control Cultures	Frit Cultures	Frit Cultures, % of Control
Total weight per pot of flowering shoots (gms.)	19.0	48.4	254	44.9	66.0	146	16.1	63.1	454
Average weight of flowering shoot (gms.)	11.1	15.4	133	15.1	19.5	128	13.3	17.9	135
Average length of stem of flowering shoot (cms.)	21.7	24.0	110	31.5	31.8	101	12.1	28.2	233

stage. The plants were removed from the culture pots, the shoots in the process of development were counted and the tops and roots of each plant were weighed separately. The data thus obtained are presented in tables 5 and 6.

Examination of the data in table 5 discloses that the number of developing shoots per plant at the end of the experiment was greatest for the frit-borne plants grown at pH = 7.0 and decreased with the increased acidity of the nutrient solution. The plants produced by the *corresponding* control cultures were in very poor condition, and an average of less than one developing flower shoot per plant was observed. However, at pH = 4.0, which produced the poorest of the *corresponding* control plants, the number of developing flower shoots was somewhat greater. When the average number of shoots per plant grown in the frits was computed as a percentage of the number produced by the *corresponding* control cultures, the relative increase due to the contact of the roots with the frit rapidly increased

TABLE 4. *Fresh weight and length of flowering shoots cut from plants grown in absolute control cultures supplied with nutrient solutions maintained at various pH values and containing adequate iron and manganese.*

TYPE OF DATA	pH VALUE OF NUTRIENT SOLUTION		
	pH = 4.0	pH = 5.5	pH = 7.0
Average total weight per pot of flowering shoots (gms.)	0	52.9	69.1
Average weight of flowering shoot (gms.)	0	19.2	18.4
Average length of stem of flowering shoot (cms.)	0	30.8	27.2

as the pH value of the nutrient solution approached neutrality. This increase indicates the influence of the frit on lessening the unfavorable effect of the higher pH values on the growth of the plants.

The greatest weight of tops obtained at the conclusion of the experiment was produced by the frit-borne plants grown at pH = 5.5. The value was insignificantly smaller at pH = 7.0, but was considerably less at pH = 4.0. The weight of the tops produced by the *corresponding* control culture of each frit always was much smaller than that produced by the frit cultures. When the weights of the frit-borne plants were computed as percentages of those produced by the *corresponding* control cultures, the data in table 5 show that the favorable effect of the frit was relatively greater when the nutrient solution was maintained at pH = 7.0.

The average weight of the roots was greater for the frit-borne plants when the pH value of the nutrient solution was 7.0. The weights produced at pH = 4.0 and pH = 5.5 were about equal in magnitude. On the other hand, the amount of root growth produced by the *corresponding* control cultures decreased with the increased pH value of the nutrient solution. A comparison of the root growth produced

TABLE 5. *Number of developing shoots, and the fresh weights of the tops, roots, and whole plants grown for four months in frit and corresponding control cultures supplied with nutrient solutions of various pH values. The data represent average values obtained from six cultures.*

TYPE OF DATA	pH VALUE OF NUTRIENT SOLUTION								
	pH = 4.0			pH = 5.5			pH = 7.0		
	Control Cultures	Frit Cultures	Frit Cultures, % of Control	Control Cultures	Frit Cultures	Frit Cultures, % of Control	Control Cultures	Frit Cultures	Frit Cultures, % of Control
Number of shoots	1.2	2.7	225	0.7	3.2	459	0.8	4.0	500
Weight of top (gms.)	31.9	50.6	159	42.3	57.8	136	28.3	56.8	201
Weight of root (gms.)	45.5	47.7	105	38.3	46.9	122	34.6	52.6	152
Total weight of plant (gms.)	77.4	98.3	176	80.6	104.8	130	62.9	109.4	174

in contact with the frits calculated as a percentage of that produced by the *corresponding* control culture shows that the effect of the frit was relatively greater as the pH value of the nutrient solution increased.

The total weight of tops and roots produced by the frit cultures increased with the increased pH values of the solution but that produced by the *corresponding* control cultures was greatest at pH = 5.5, smaller at pH = 4.0, and smallest at pH = 7.0. When the percentage values were calculated, the favorable effect of the frit on the total weight of the plants was relatively smaller at pH = 5.5 and greater at the highest and lowest pH values.

It is apparent from a comparison of the data in table 5 with those in table 3 that the number and quality of the flowering shoots produced is positively related to the weight of the tops but not necessarily to the weight of the roots.

TABLE 6. *Number of developing shoots, and the fresh weights of the tops, roots, and whole plants grown for four months in absolute control cultures supplied with nutrient solutions of various pH levels and which contained adequate amounts of iron and manganese. The data represent average values obtained from six cultures.*

TYPE OF DATA	pH VALUE OF NUTRIENT SOLUTION		
	pH = 4.0	pH = 5.5	pH = 7.0
Number of shoots	0	4.0	3.0
Weight of top (gms.)	0	73.8	55.4
Weight of root (gms.)	0	48.8	56.4
Total weight of plant (gms.)	0	122.6	111.8

The data in table 6 were obtained from the rose plants grown in the *absolute* control cultures maintained at the different pH values and which received adequate amounts of soluble iron and manganese. All plants growing at pH = 4.0 had died by the time the experiment was terminated, however, the plants grown at the higher pH values were still developing shoots and producing flowers. The number of developing shoots, weight of the top, and of the total plant was greater when the pH value of the nutrient solution was maintained at 5.5 than at 7.0. A comparison of the data in table 6 with those in table 5 shows that the contact of the roots with the frit considerably lessened the injurious effects of the more acid nutrient solutions. Again it appears that the quality of the top according to commercial standards is not related necessarily to the weight of the roots. In general, the data show that the *absolute* control cultures produced somewhat larger plants than did the frit cultures, but the increase is too small to merit emphasis.

D. IRON AND MANGANESE CONTENT OF THE LEAVES

The data described in the preceding sections show that the best roses as judged by commercial standards were produced by the frit

TABLE 7. *Concentration of iron and manganese, expressed as parts per million, in the dry leaves of rose plants grown in frit and corresponding control cultures and supplied with nutrient solutions maintained at various pH values.*

pH OF NUTRIENT SOLUTION	CULTURE NUMBER	IRON			MANGANESE			FE: MN RATIO		
		Control Cultures	Frit Cultures	Frit Cultures, % of Control	Control Cultures	Frit Cultures	Frit Cultures, % of Control	Control Cultures	Frit Cultures	Frit Cultures, % of Control
4.0	1	77	81	103	619	545	89	0.124	0.149	120
	2	78	73	93	597	496	83	0.131	0.147	112
	3	96	96	100	783	525	67	0.123	0.183	148
	Ave.	84	83	99	666	522	79	0.126	0.160	124
5.5	1	82	100	122	880	553	63	0.093	0.181	194
	2	68	85	125	846	611	72	0.080	0.139	174
	3	72	82	114	862	692	80	0.084	0.118	141
	Ave.	74	89	120	863	619	71	0.086	0.146	169
7.0	1	65	77	119	523	450	86	0.124	0.171	138
	2	67	78	116	542	493	91	0.124	0.158	126
	3	64	79	123	555	456	82	0.115	0.173	150
	Ave.	65	78	120	540	466	86	0.121	0.167	138

supplied with nutrient solution maintained at pH = 5.5. Further, the relative difference between the number and quality of flowers produced by the frit and by its *corresponding* control culture became progressively greater as the pH value of the nutrient solutions increased. Although the frit greatly lessened the injurious effects of the extreme high and low acidities of the nutrient solutions, the effect of an unsatisfactory pH value of the medium was not entirely eliminated for slightly better plants were grown at pH = 5.5.

Since the frit had been compounded on the basis of previous experiment to release iron and manganese, it is interesting to observe the actual concentrations of these nutrients in the leaves of the plants, and especially to observe how these concentrations are related to the quality of the plants and flowers. Consequently, the leaves remaining on the plants at the end of the experiment were dried, finely ground, and analyzed as described below.

The fresh leaves were washed in 0.05 normal hydrochloric acid, dried at 60° C. in a forced-air chamber, and ground in a laboratory mill to pass a 40-mesh screen. One-gram samples of the powered material were ignited in platinum crucibles for two hours in an electric muffle at 850° C. After cooling, the ash was moistened with one milliliter of dilute sulphuric acid and then five milliliters of hydrofluoric acid were added. The sample was evaporated on an electric hot plate until the residue attained a viscous consistency. About ten milliliters of a 0.1 normal nitric acid were then added to the crucible while still on the hot plate, the warm solution transferred to a 50-milliliter volumetric flask, and brought to volume with 0.1 normal nitric acid. Iron was determined in aliquots of the dilute ash solution by the colorimetric procedure described by Hummell and Willard (1938). Manganese was determined by the colorimetric procedure described by Willard and Greathouse (1917).

Concentration of iron in the leaves. The data showing the concentrations of iron in the leaves are presented in table 7. When the average values are considered, it appears that more iron was present in the leaves of the best plants, that is, in those grown on the frit with a nutrient solution at 5.5. A little less iron was found in the leaves when the pH value of the nutrient solution was pH = 4.0, and still less when it was maintained at 7.0. In other words, the concentration of iron found in the leaves did not vary as the quality of the plants varied, nor as the pH value of the nutrient solution varied. The explanation of this situation is to be found in the relationship of iron to manganese described in a later section of this report.

When the iron contents of the leaves of the frit-borne plants are calculated as percentages of those in the *corresponding* control plants, it is seen that both cultures produced plants containing about the same concentration of iron in their leaves when the nutrient solution was maintained at pH = 4.0, but the concentration was 20 percent higher than in the *corresponding* controls when the solutions were maintained at the pH values of 5.5 and 7.0.

This increase probably was due to the fact established by previous experiments that the iron in the frit was soluble to an almost infinitesimal degree in acid solutions. Consequently in the most acid nutrient

solution used in the experiment, the solubility of the iron in the frit was sufficiently great to permit the *corresponding* control cultures to receive comparatively large amounts of iron from the solution which flooded simultaneously the corresponding frit cultures.

If the control cultures alone are considered, the concentrations of iron in the leaves increase as the acidity of the nutrient solutions increased. This situation again suggests a certain solubility of the iron in the frit, and also a relationship between this solubility and the pH value of the solution because these *corresponding* control cultures received only such amounts of iron as were dissolved from their adjoining frit cultures. The minute solubility of iron was not related to the quality of the plants produced as the plants grown at pH = 4.0 were in very poor condition at the end of the experiment, while those grown at pH = 5.5 were still healthy and producing normal flowers. This inconsistency between the amounts of iron released from the frit through its solubility and the quality of the plants produced may be explained by the fact that manganese also was released and at rates widely differing

TABLE 8. *Concentrations of iron and manganese in the nutrient solutions after two months of periodic leaching through the frit cultures. The data represent averages obtained from six duplicate carboys.*

pH VALUES OF NUTRIENT SOLUTION	MILLIGRAMS PER CARBOY OF NUTRIENT SOLUTION		PARTS PER MILLION IN THE NUTRIENT SOLUTION		IRON: MANGANESE RATIO
	Fe	Mn	Fe	Mn	
4.0	7.1	273	0.44	17.0	0.026
5.5	5.5	180	0.34	11.3	0.031
7.0	5.3	22	0.33	1.4	0.241

from those of iron. Further, the pH value of the most acid *absolute* control solution is shown by the data in table 6 to have been intrinsically toxic, quite independently of the soluble iron which it contained.

Concentration of manganese in the leaves. The concentration of manganese in the leaves are shown by the data in table 7. The leaves of the best rose plants, namely those grown on the frit supplied with nutrient solution maintained at pH = 5.5, contained the greatest concentration of manganese. When the pH value of the nutrient solution was 4.0, the leaves contained smaller concentrations of manganese, and still smaller concentrations at pH = 7.0. Also as with iron, the accumulations of manganese in the leaves did not vary directly with the commercial quality of the plants nor with the differences in the acidities of the nutrient solutions.

The concentrations of manganese in the leaves calulated as percentages of those in the *corresponding* control plants showed that the best plants contained only 71 percent as much as their corresponding controls. The plants of intermediate quality, that is those grown at pH = 7.0, contained 86 percent as much, while in the poorest plants,

grown at pH = 4.0, the percent was 79. Qualitatively, the same situation existed with respect to iron. The quality of the plants was not related directly to the pH value of the solution nor to the concentration of manganese in the leaves.

The amounts of manganese found in the leaves of the *corresponding* control plants do not show the same relationships as did iron. For example, these leaves contained either the same amount of iron or less than did those produced by the corresponding frit cultures. The extent of this diminution became greater as the nutrient solutions were more alkaline. In the case of manganese, however, the leaves produced by the *corresponding* control plants always contained significantly greater amounts than did those of the plants grown in the corresponding frit cultures!

The problem immediately arises as to why the *corresponding* control plants absorbed so much more manganese than the frit-borne plants when the control plants had access only to the soluble manganese released from its adjacent frit culture and the frit-borne plants on addition to this supply were growing in direct contact with the frit. The answer to this perplexing problem probably lies in the relationship known to exist between the absorptions of iron and manganese. Previous experiments have shown that the solubility of the iron in the frit was extremely low, while that of manganese was relatively high. The solubilities of both vary as does the hydrogen ion concentration of the solution, but to very different degrees. This situation means that the leachate from the frit, represented in the experiment by the nutrient solution, would contain more manganese than iron and would become unbalanced or even toxic in its effect on growth. The degree of this unbalance would depend on the pH value of the solution since the effect of the pH on the solubility of manganese is very much greater than on the solubility of iron.

To return to the problem at hand, the plants growing in the *corresponding* control cultures had access to the relatively high amounts of soluble manganese, but the available soluble iron was so low that toxic amounts of manganese were absorbed. On the other hand, even though the plants growing on the frit had access to the same amount of soluble manganese and also to that available through root contact with the frit, these plants in addition had access to iron by root contact with the frit. The additional iron thus available apparently was adequate to depress the absorption of manganese to a non-toxic level, or at least to induce a more favorable iron:manganese ratio in the plants.

It will be recalled that the plants grown in the *corresponding* control cultures became chlorotic to varying degrees during the course of the growing period even though chemical analysis showed them to contain considerable, and probably intrinsically adequate, amounts of iron. It is reasonable to assume that this chlorosis was due primarily to the excessive absorption of manganese rather than to the comparatively small absorption of iron.

Iron : manganese ratio in the leaves. The ratios of the concentrations of iron to manganese in the leaves of the rose plants are presented in table 7. These data are consistent with the theory presented above that the best plants were obtained under conditions which not only

permitted an adequate absorption of iron *per se*, but also enough to prevent the excessive absorption of manganese. The lowest iron : manganese ratio existed in the leaves of the best plants which were grown at pH = 5.5. The frit-borne plants grown at this pH value exhibited a ratio of 0.146 which appears to be a satisfactory value for roses grown under the conditions of the experiment.

The leaves of the plants grown in the *corresponding* control cultures exhibited a ratio of only 0.086. At all pH values of the nutrient solution, the smaller iron : manganese ratios occurred in the *corresponding* control plants indicating that these plants always absorbed relatively more manganese with respect to iron than the corresponding frit-borne plants; this we can only ascribe to the greater availability of iron in the frit cultures, especially as the data in table 7 show the significantly greater concentration of iron in the most satisfactory plants which were grown on the frit supplied with nutrient solution at pH = 5.5.

IV. Discussion

The data assembled in table 8 show the concentrations of iron and manganese in the nutrient solutions after they had flooded the frits at 4-hour intervals for period of two months. The effects of the pH values on the amounts of iron and manganese in the solutions are clearly evident, and the differences in the solubility of iron and manganese are especially apparent. The amounts of iron accumulating in the solutions were very small and varied only from 0.44 to 0.33 parts per million. The total amount of iron released to the carboys of nutrient solution varied from 7.1 to 5.3 milligrams. During the same period, from 17.0 to 1.4 parts per million of manganese accumulated in the solution or from 273 to 22 milligrams per carboy.

These data show that the iron in the frit is very insoluble even at the more acid pH values of the solution, for certainly 7.1 milligrams is a small amount to be dissolved by 360 successive leachings of 18 liters of solution through one gallon of the frit. Consequently, it appears unlikely that the robust development of the rose plants could have been made possible by iron dissolved from the frit. On the other hand, 273 milligrams of manganese were dissolved in the nutrient solution under the same conditions. This comparatively large amount is more than adequate to support normal plant growth and one must conclude that the fine plants produced by the cultures at pH = 5.5 need not have been conditioned necessarily by contact absorption of this nutrient.

Previous experiments with wheat plants have shown that excellent growth was obtainable by the use of frit containing iron (but *not* manganese) at all pH values of the solution from 4.0 to 7.0. The present data show that the effect of varying the pH value from 4.0 to 7.0 caused the concentration of iron in the solution to decrease insignificantly, namely from 0.44 to 0.33, or only 0.11 part per million. As far as iron alone is concerned, the pH value of the solution exerts but little effect, apparently because the iron in the frit is absorbed by the plants almost exclusively through root contact with it.

A very different situation exists with respect to manganese for the data in table 8 show not only that it was very much more soluble

than iron, but also that the pH value of the solution exerted a significant influence on its solubility. When the pH was maintained at 4.0, 17.0 parts per million of manganese were released, while only 1.4 were released at pH = 7.0. These large amounts together with the pronounced effect of pH on their magnitudes, make the maintenance of a favorable pH value of the nutrient solution far more important when the frit contains both iron and manganese than when manganese is lacking.

When it is recalled that the nutrient solution maintained at pH = 5.5 produced eminently satisfactory rose plants and yet accumulated only 0.34 part per million of iron, but 11.3 parts per million of manganese one might wonder how a nutrient solution so far out of balance with respect to these nutrient could function so satisfactorily. Certainly if soluble salts of these nutrients were added to the solution in this ratio, the effect would be toxic. The lack of toxicity observed in the present experiment could only have been due to the high availability of iron to the plants through root contact with the frit.

If the above interpretation is correct, one would expect, as was pointed out earlier in the discussion, that the plants growing in the *corresponding* control cultures would not thrive for they received large amounts of manganese through its solubility in the solution draining into the common carboy from the corresponding frit culture. Since these plants had no contact with the frit, sufficient iron available to balance the physiological effect of the manganese.

The data in table 8 also show that the nutrient solutions of the cultures producing the best growth and quality of roses accumulated iron and manganese in a ratio of 0.031. This value varies so greatly from those known to produce satisfactory plant growth in hydroponic cultures that again one must assume the importance of the absorption of iron by direct contact of the roots with the frit.

The above discussion suggests the possilility of using iron-containing frit to counteract the toxic effect of excess manganese in some unusual tropical soils for both the frit cultures and their *corresponding* control cultures received excessive amounts of manganese through its solubility in the solution flooding both culture pots. The plants growing in the quartz suffered from manganese toxicity, while those growing in the frit were normal in every way because of the balancing effect of the iron that was absorbed by direct root contact with the frit.

V. Summary and Conclusions

1. A major difficulty encountered in the commercial hydroponic culture of roses is the maintenance of an adequate supply of soluble iron and manganese in the nutrient solution. Several investigators have used various materials as a solidphase source of iron. The present study shows the usability of glassy frit as a source of iron and manganese to roses. Pairs of cultures were arranged to permit a differentiation between the availability of iron and manganese due to their solubility and due to root contact with the frit. The effect of the pH value of the nutrient solution on the response of the plants to the frit also was investigated. The visual appearance of the plants, growth, yield offlowers, and the iron and manganese contents of the leaves were reported.

2. The frit-borne plants were equal, or superior, to those grown in complete nutrient solutions containing adequate amounts of soluble iron and manganese. Normal green plants were obtained with pH values of the nutrient solution varying from 4.0 to 7.0. Slightly better plants, however, were obtained when the pH was maintained at 5.5. Corresponding control cultures produced chlorotic plants, the chlorosis being most severe at pH = 7.0.

3. The rose plants were conspicuously more tolerant of wide variations in the pH value of the nutrient solutiom when their roots were in contact with the frit. Under commercial conditions, pH values from 5.0 to 6.0 would be eminently satisfactory, and even more extreme values would not seriously lessen the value of the crop.

4. Data are presented to show that the absorption of iron by by the plants depended primarily on the physical contact of their roots with the frit. The solubility of manganese was conspicuously greater than of iron and consequently the relative magnitude of its availability to the plants root contact and by its solubility could not be determined as decisively as in the instance of iron.

5. Chemical analyses of the leaves and the nutrient solutions showed the greater importance of the pH value of the solution when when frit containing both iron and manganese was used than when manganese was lacking.

6. The toxic effect of excessive manganese in the nutrient solution was eliminated when the roots were in contact with the frit. The use of an iron-containing glass frit as a means of eliminating the effect of excess available manganese in tropical soils was suggested.

VI. LITERATURE CITED

Hummell, F. G., and **Willard, H. H.** Determination of iron in biological materials. Ind. Eng. Chem., Anal. Ed. **10:** 13–15. 1938.

Shive, J. W. A three salt solution for plants. Am. Jour. Bot. **2:** 157–160. 1915.

Somer, I. I., and **Shive, J. W.** The iron-manganese relation in plant metabolism. Plant Physiol. **17:** 582–603. 1942.

Stromme, E. R., and **Wynd, F. L.** The influence of the pH value of the medium on the availability to plants of iron and manganese in glass frits. Lloydia **16:** 1–58. 1953.

Willard, H. H., and **Greathouse, L. W.** The colorimetric determination of manganese with periodate. Jour. Am. Chem. Soc. **39:** 2366–2377. 1917.

Wynd, F. L. The use of iron-containing frit as a new medium for hydroponic culture. Mich. Agri. Exp. Sta., Quart. Bul. **33:** 52–53. 1950.

Wynd, F. L. Availability to wheat of iron in very insoluble glass frits. Lloydia **14:** 1–33. 1951.

Wynd, F. L., and **Stromme, E. R.** Absorption of manganese and iron by Navy bean plants grown in a calcareous soil fertilized with a manganese-containing glassy frit. Lloydia **14:** 39–54. 1951.

Wynd, F. L., and **Bowden, Roy A.** Response of Snapdragons to very insoluble iron-containing frit. Lloydia **14:** 33–39. 1951 (a).

Wynd, F. L., and **Bowden, Roy A.** Response of chlorotic Blueberry bushes to a very insoluble iron-containing glassy frit. Lloydia **14:** 55–57. 1951 (b).

Availability to Soybeans of Iron in Several Relatively Insoluble Substances[1]

F. L. Wynd[2]

I. Introduction

The availability to plants of iron in relatively insoluble substances has been investigated by several workers. For example, Eaton (1936) stated that 0.1 percent of magnitite mixed with quartz sand permitted normal growth of plants if the nutrient solution was maintained on the acid side of neutrality. Eaton pointed out, however, that different species of plants varied in their ability to obtain an adequate supply of iron from the magnitite when the pH value of the nutrient solution approached neutrality. Only exceptional species obtained sufficient iron if the solution became as alkaline as pH = 8.0.

Chapman (1939) reported that citrus seedlings grew satisfactorily in quartz gravel mixed with magnitite if the nutrient solution was maintained at pH values from 5.8 to 7.0. If calcium carbonate was added to the cultures, the amount of magnitite had to be increased in order to obtain satisfactory plants. This situation suggested that the extent of the physical contact of the magnitite with the roots must be increased as the pH value of the nutrient solution increased. Guest (1944) used a mixture of bentonite and magnitite as a source of iron for citrus. Like Chapman, he found that the total surface of magnitite in the culture must be increased if the pH value of the nutrient solution became alkaline. The use of a more finely ground material produced the required increase in surface just as efficiently as the addition of larger amounts of magnitite. Finely ground dolomite caused chlorosis to appear, but this was believed to be due to the mechanical prevention of adequate root contact with the magnitite rather than to the effect of the resultant pH value of the solution.

Certain sands also have been shown to release iron to plants. Eaton (1936) showed that ordinary beach sand usually supplied an adequate amount of iron to plants from the insoluble compounds which it contained. Eaton concluded that the plants obtained iron from insoluble compounds by particle-root contact rather than from the extremely small soluble iron fraction. Even corn, a plant known to have an unusually high iron requirement, obtained an adequate amount of this nutrient from the beach sand used in his experiments.

Ellis and Swaney (1938) also expressed their opinion that plants could obtain a sufficient amount of iron from most sands. However, their experiments showed that the addition of soluble iron compounds to hydroponic cultures was necessary to obtain normal plant growth if the purer grades of silica or quartz sands were used.

---

[1]The expenses incurred during this investigation were borne by a grant-in-aid provided by the Ferro Corporation, Cleveland, Ohio.

[2]Research Professor, Department of Botany and Plant Pathology, Michigan State College, East Lansing, Michigan.

The use of glass wool as a source of slowly available iron to plants was suggested by Slayter and Thomas (1940). These investigators stressed the advantageous use of glass wool "as a covering or protective component in the soil, particularly at a time when the ground is bare." The glass wool also was believed to act as a "fertilizer or conditioner of the soil" because of "certain novel compositions of ingredients of the glass." The legal verbiage of the extensive claims presented by Slayter and Thomas is difficult to interpret from the viewpoint of the nutritional requirements of plants, but in general, the use of their glass wool for agricultural purposes was based on the following properties:

A satisfactory composition of the glass, expressed as percentages, was stated as follows:

P_2O_5	25 to 50
SiO_2	0 to 30
K_2O	15 to 30
CaO	20 to 30

In addition to the above components, small amounts of Na_2O, MgO, SO_3, ect., also were believed to impart beneficial fertilizer qualities to the glass. The availability of the nutritionally significant components in the glass wool was believed to be due to a certain solubility brought about by weathering, for they stated, "The destruction and disintegration of this glass under weathering proceeds at a moderate rate, particularly if there is a constant temperature cycle to which the glass is subjected".

The meanings of the phrases "constant temperature cycle," "destruction and disintegration," and "moderate rate" are not clearly apparent. Temperature could not be constant and yet represent a cycle. Does the phrase mean a constant temperature, or a recurring cycle of temperature changes? Is it to be inferred that the availability to plants of the iron in the glass depends on a specific temperature phenomenon? Destruction and disintegration also are vague terms. It is known that some kinds of glass disintegrate in water, becoming thereby a suspension of finely divided colloidal particles. Disintegration in this sense is not the equivalent of aqueous solubility in the physiological sense because plant roots are unable to absorb colloidal particles. Does iron in the glass wools of Slayter and Thomas become available through direct root contact with the colloidally dispersed particles, or through the aqueous solubility of the iron itself? It is evident that the authors presumed that the availability of the iron in glass wool depended on some kind of solubility or disintegration of the material. The effect of the weather on the process is implied.

It is not the purpose of the present writer to question the effectiveness of glass wool as a fertilizer for plants but rather to point out that the explanation of the mechanism of its effectiveness leaves much to be desired.

Matlin (1942) stated that the use of pumice gravel as the supporting matrix in hydroponic cultures supplied not only sufficient iron to plants but also significant amounts of other plant nutrients although it should be pointed out that his statement, "Pumice rock also contains such a large amount of plant food that very little has to be added for success-

ful plant growth," was not supported by data. His statement that pumice owed its effect on plant growth to its "unique chemical and physical properties" also was made without any attempt to describe or define these properties. The following average composition of pumice, expressed as percentages, was presented, but a critical study of the availability of the specific nutrient ions was not described:

SiO_2	70.90	MgO	0.24
Al_2O_3	15.20	TiO_2	0.02
Na_2O	5.85	Mn_2O_3	0.02
K_2O	2.70	BaO	0.01
Fe_2O_3	0.80	B_2O_3	0.01
CaO	0.66		

Badger and Bray (1945) described the possibility of using especially compound glasses as sources of nutrients for plants. These investigators were the first to define the properties of their experimental materials. They assumed that the availability to plants of certain components of the glass depended on their aqueous solubilities. Consequently they made an extensive study of the relationship between the solubility of the potassium and phosphate ions and the composition of the glass. The effect of various smelting temperatures also was investigated.

Badger and Bray limited their studies to the solubilities of potassium and phosphate ions, although they postulated the possibility of incorporating all essential plant nutrients except nitrogen in soluble form in glasses. Nutritional experiments with plants were not performed, however.

The above review of the pertinent literature discloses that the use of relatively insoluble substances as sources of iron for plants has long been regarded as feasible. All authors excepting Eaton have assumed that the nutritional important ions in their materials became slowly available through their aqueous solubilities. Only Badger and Bray attempted to define specific properties of their materials and conditions of their manufacture. None of the authors cited above has presented critical data showing actual availabilities of nutritional ions in their materials to growing plants.

The present writer was permitted to reinvestigate the possibility of using glass frits as sources of nutrients to plants through the generosity of the Ferro Corporation of Cleveland, Ohio. The results of these investigations (Wynd, 1950, 1951, 1952a; Wynd and Bowden, 1951a, 1951b; Wynd and Stromme, 1951; Stromme and Wynd, 1953) have shown that iron and manganese can be supplied in optimum quantities to plants by bringing their roots in contact with properly compounded glass frits. One of the most interesting observations made was that the availability of iron to the experimental plants was not related to its solubility. In fact, the best of the many frits studied always were those exhibiting the lowest solubilities. In all cases, prolonged leaching failed to extract sufficient iron from the superior frits to support normal plant growth.

The evidence presented in the several papers of Wynd and his coworkers showed that the iron was available to the plant roots through their physical contact with the frit particles. The nature of the frit matrix influenced to a marked degree the amount of iron released to

the plants, but the variations in the availability were not related to the observed differences in the aqueous solubilities of the frit. These studies therefore differed significantly from those reported previously in the literature for they led to the production of satisfactory frits based strictly on the release of iron to plants through root contact rather than by aqueous solubility.

Specific data have not been published showing the availability of iron to plants in the relatively insoluble substances described by previous workers. Consequently, the present experiment was designed to compare the effectiveness of those substances with that of one of the frits developed by the present writer.

II. Experimental Methods and Materials

A series of 1-gallon glazed earthenware pots were arranged as described by Wynd (1951). Duplicate cultures were used to study the iron-supplying ability of each of the materials described below. Magnitite was mixed with purified quartz gravel to give a concentration of 0.1 percent by weight of Fe_3O_4 as suggested by Eaton (1936). Glass wool was loosely packed in another pair of culture pots as recommended by Slayter and Thomas (1940). Pumice gravel graded to fragments about one-fourth of an inch in diameter was used as suggested by Matlin (1942). Magnitite also was added to dolomite gravel graded to a particle size of one-fourth of an inch.

Each pair with culture pots was flooded at four-hour intervals with the nutrient solution described by Wynd (1951). The solutions contained all nutrients known to be essential for the growth of green plants excepting iron. The pH values of the solutions were maintained at 5.5 excepting of course the solution flooding the culture containing dolomitic limestone.

Soybeans were germinated in purified quartz sand. As soon as the seedlings were large enough to be handled, their cotyledons were removed with a razor blade. Five seedlings were then carefully established in each of the culture pots.

The glass frit used was designated as number 9140-1 in an earlier report (Wynd, 1950b). Its composition, expressed as percentages, was as follows:

SiO_2	72.60	K_2O	8.09
CaO	6.16	Na_2O	8.09
MgO	4.05	Fe_2O_3	1.01

The aqueous solubility of this frit, as determined by standard procedures, was 4.1 percent, a value which is only about 2.5 times that obtained by similar procedures from a commercial soft drink bottle.

The iron contents of the various materials studies,expressed as percentages of Fe_2O_3, were found by analysis to be as follows:

Frit No. 9140–1	1.01
Magnitite	80.71
Glass wool	0.13
Pumice	1.51

PLATE 1. Terminal portions of soya bean plants grown in hydroponic cultures supplied with various kinds of relatively insoluble iron-containing materials. From left to right: glass wool, quartz sand plus 0.1 percent magnitite; quartz sand plus 50 percent fine pumice gravel; dolomitic gravel plus 0.1 percent magnitite; glass frit A–9140–1.

III. Experimental Results

The differences in the color of the foliage of the experimental plants became increasingly pronounced during the course of their vegetative development. The experiment was terminated when the flower buds became evident.

It is well known that the growing, terminal leaves of plants are especially sensitive to iron deficiency. Consequently the tips of the plants were cut off just below the uppermost fully expanded leaf, pinned against a light-gray background, and Kodachrome photographs taken. The effects of the various insoluble iron-containing components in the culture pots are evident in plate 1.

Very chlorotic plants resulted when iron supplied in glass wool, magnitite, and pumice. On the other hand, the vivid green color of the terminal portion of a plant grown in the especially compounded glass frit shows that the soya bean plants received an adequate amount of iron from this material. It should be pointed out also that the plants growing in the frit continued their normal development, while those depending on glass wool, pumice, or magnitite for their supply of iron finally died before their flowers were fully open.

IV. Summary and Conclusions

Soya bean plants were grown in hydroponic culture. Iron was supplied by glass wool, pumice, magnitite, and a specially compounded glass frit.

The plants growing in the glass frit were vividly green in color and produced flowers normally. All plants supplied with the remaining types of iron-containing materials became severely chlorotic and died before their flowers were fully opened.

The glass frit contained 1.01 percent of iron expressed as Fe_2O_3 and its aqueous solubility was 4.1 percent as determined by a standard procedure for determining the solubility of glass. This solubility was only 2.5 times that of a commercial soft drink bottle.

V. LITERATURE CITED

Badger, A. E., and **R. H. Gray.** 1945. Soluble glass may offer fertilizer possibilities. Chem. and Met. Eng., April, pp. 112–13.

Chapman, H. D. 1939. Absorption of iron from finely ground magnitite by Citrus seedlings. Soil Sci. **48:** 309–317.

Eaton, F. M. 1936. Automatically operated sand-culture equipment. Four Agr. Res. **53:** 433–444.

Ellis, C., and **M. W. Swaney.** 1938. Soilless growth of plants. Reinhold Publishing Corporation, N. Y.

Guest, P. L. 1944. Root contact phenomena in relation to iron nutrition and growth of Citrus. Proc. Ann. Soc. Hort. Sci. **44:** 43–48.

Matlin, D. R. 1942. Chemical Gardening. Chemical Publishing Company, Brooklyn, N. Y.

Slayter, Gaines, and **John H. Thomas.** 1940. Agricultural application of glass wool. U. S. Patent No. 2,192,939. March 12.

Stromme, E. R., and **F. L. Wynd.** 1953. The influence of the pH value of the medium on the availability to plants of iron and manganese in glass frits. Lloydia **16:** 1–58.

Wynd, F. L. 1950. The use of iron-containing frit as a new medium for hydroponic cultures. Mich. Agr. Exp. Sta., Quart. Bul. **33:** 52–53.

Wynd, F. L. 1951. Availability to wheat plants of iron in very insoluble glassy frits. Lloydia **14:** 1–33.

Wynd, F. L. 1953. Glass frit as a source of iron and manganese for roses grown in hydroponic culture. Lloydia **16**: 59–76.

Wynd, F. L., and **R. A. Bowden.** 1951a. Response of snapdragons to very insoluble iron-containing frit. Lloydia **14**: 34–39.

Wynd, F. L., and **R. A. Bowden.** 1951b. Response of chlorotic blueberry bushes to a very insoluble iron-containing glassy frit. Lloydia **14**: 55–57.

Wynd, F. L., and **Erling Rein Stromme.** 1951. Absorption of manganese and iron by navy bean plants grown in a calcareous soil fertilized with a manganese-containing glassy frit. Lloydia **14**: 40–54.

A Study of the Accuracy of the Buffer Procedure for Determining the Lime Requirements of Soils[1]

F. L. Wynd[2]

Table of Contents

I. INTRODUCTION

The lime requirement of a soil is defined as the amount of lime required per acre to neutralize the hydrogen ions adsorbed on the surfaces of the soil colloids. The laboratory determination of the lime requirement consists of two distict processes. The first is the replacement of the colloidally-bound hydrogen by another species of ion in the extracting solution, and the second is the quantitative determination of the amount of hydrogen thus released to the extracting solution. Obviously, the magnitude of the lime requirement of a soil may not be determined from the pH value of its aqueous suspension.

Superficially, both phases of the determimation of the lime requirement appear to be simple processes, but actually each is fraught with considerable difficulty. The quantitative replacement of the colloidally-bound hydrogen is especially difficult for the process often approaches equilibrium slowly and proceeds at widely-different rates in different soils. Soils exhibiting a high lime requirement, and therefore requiring especially precise determinations, are particularly troublesome in this respect. The determination of the amount of hydrogen replaced must be done with accuracy under the difficult conditions imposed by the extracting solution for an error amounting to only 0.001 gram of hydrogen in a ten-gram sample of soil corresponds to an error of 1,000 pounds per acre of pure calcium carbonate, or to 1,250 pounds of the standard "agricultural grind" limestone.

The research chemist, aided by adequate equipment and patience, can obtain very accurate determinations of the amount of replaceable hydrogen in soils and consequently of their lime requirements, but laboratory workers confronted with the necessity of reporting on innumerable samples of soil for a pitifully inadequate fee face a very real problem. The farmer is not accustomed to paying for the comparatively expensive but accurate procedures, and the laboratory

[1]The expenses of this investigation were borne jointly by the Greenmelk Company, Ltd., Wallaceburg, Ontario, and the Cerophyll Laboratories, Inc., Kansas City, Missouri.

[2]Research Professor, Department of Botany and Plant Pathology, Michigan State College, East Lansing, Michigan.

workers cannot give him accurate data by most of the abbreviated "quick tests" which he is forced to use.

Necessity has pressed the soil chemists to develop rapid and inexpensive methods for determining the lime requirements of soils. Many such methods have been proposed ranging from procedures which are almost adequate to those which absurdly use the pH value of a water suspension of the soil. The usefulness of rapid procedures for determiming lime requirements of soils is so great that any reasonable proposal should be investigated thoroughly with the hope that it will at last be the answer to one of the most important problems facing those who must advise farmers how much lime their soils require.

One such proposal is the use of buffer solutions possessing certain properties. Such a procedure involves agitating a measured amount of soil with an aliquot of the buffer solution and then determining the lime requirement of the soil from the change observed in the pH value of the buffer, this change being brought about by the hydrogen released from the soil colloids by certain ions in the solution. The use of a buffer solution for this purpose is almost as simple and rapid as the determination of the pH value of a suspension of the soil in water.

Brown (1943) was the first to suggest agitating a sample of soil in a buffer solution in order to estimate its lime requirement. This investigator used neutral, 1-normal ammonium acetate. Actual titration curves showed that the addition of acid hydrogen sufficient to change the acidity of this buffer 0.1 of a pH unit corresponded to a lime requirement of 1,000 pounds of calcium carbonate per acre.

The ammonium ion frequently is used as a replacing agent for the determination not only of hydrogen but also of other bases adsorbed on the soil colloids, but its satisfactory use for this purpose depends on the slow leaching of the soil sample with *successive* portions of the solution. The higher the base exchange capacity, the more essential it becomes that the leaching process proceed *slowly* and with *successive* portions of the solution. In view of these precautions so well known by soil chemists to be necessary for the complete leaching of the exchangeable ions from soil by ammonium acetate, it seems hardly likely that an adequate extraction of exchangeable hydrogen could be obtained merely by shaking the sample for a short period with one aliquot of the solution.

However, the ammonium acetate buffer proposed by Brown does indicate the lime requirements of many soils with usable accuracy. Brown, himself, compared the results obtained by this procedure with those obtained by the precise procedures described by Schollenberger and Dreibelbis (1930) for the determining of exchangeable hydrogen and found a satisfactory agreement of the data. The data also agreed satisfactorily with those obtained by the calcium acetate extractant described by Jones (1913) and by Merkle (1940) but since his extractant is subject to the same sources of error as ammonium acetate, the similarity of the results obtained, therefore, did not verify the accuracy of the ammonium acetate procedure.

The present writer has used the ammonium acetate buffer proposed by Brown for the determination of the lime requirements of several thousand soil samples collected from widely scattered areas in the

United States. Each determination was checked for accuracy by base exchange data obtained with all possible precision. The lime requirements obtained by the ammonium acetate buffer proved to be accurate in some instances but very inaccurate for the majority of the samples studied. The greatest errors occurred with soils of high clay content and containing comparatively large amounts of exchangeable hydrogen. Low estimates of the lime requirements were so commonly obtained that the procedure was abandoned for routine use.

Woodruff (1947, 1948) recently described an especially designed buffer solution for the determination of exchangeable hydrogen in soils, and consequently also their lime requirements. This author correctly stated the necessary properties of any buffer for its satisfactory use in determining lime requirements as follows:

1. The pH value of the buffer must change linearly with the amount of acid added to it.

2. The rate of its reaction with the exchangeable hydrogen in the soil must be rapid.

3. The behavior of the buffer must be independent of the base exchange capacity of the soil, of the type of clay minerals present and the degree of base saturation of the soil colloids.

Brown's ammonium acetate buffer did not meet the necessary conditions pertaining to the base exchange capacity, type of clay minerals present, and degree of base saturation. Since Woodruff stressed the necessity of satisfactorily meeting these conditions it would be assumed that the buffer proposed by him would be more satisfactory than that proposed by Brown. Consequently the present study was carried out in order to determine the usefulness of Woodruff's procedure.

II. EXPERIMENTAL METHODS AND MATERIALS

Samples representing many types of soils were obtained from several areas in the United States. Each sample was air-dried, ground in a mortar to pass a 1-millimeter sieve and stored in air-tight containers until subjected to analysis. The exchangeable hydrogen was determined by the difference between the base exchange capacity and the total exchangeable bases. These determinations were carried out by the methods described by Bray and Willhite (1929). Every precaution was taken to insure as high a degree of accuracy as possible as the amounts of exchangeable hydrogen in the soil indicated by these determinations were used as the standards by which the accuracy of the lime requirement determinations were judged.

The buffer solution proposed by Woodruff consisted of calcium acetate, para-nitrophenol, and magnesium oxide. The published directions for preparing the solution were followed, but a heavy precipitate always was obtained. The writer corresponded with Woodruff concerning this difficulty and every suggestion was carefully followed, but a satisfactory solution could not be prepared. Further correspondence revealed that the solution could be purchased from the Limemeter Laboratories, Columbia, Missouri, for five dollars per gallon. Rather

than pursue further the technical difficulties of preparing the solution and to make certain that a correctly prepared solution was used for the comparative tests, sufficient solution was purchased from the Linemeter Laboratories to determine the lime requirements of about 1,200 samples.

III. EXPERIMENTAL RESULTS

It is not possible to add lime to a field in amounts nearer than 1,000 pounds to the calculated amount with the type of machinery in common use. Therefore, agreements within 1,000 pounds of the theoretically perfect values were considered satisfactory in the present study.

The data assembled in table 1 indicate the lime requirements obtained by the buffer and by base exchange data for soils of different areas. Unsatisfactory agreements were obtained for all samples from the vicinity of Upperville, Virginia, while satisfactory agreements were obtained with soils from near Athens, Georgia, from Richmond, Missouri from Lake View, Kansas, and from Westchester, Pennsylvania. The errors obtained with the Virginia soils often were very large as shown by deviations as great as 6,700, 5,100 and 4,700 pounds per acre from the theoretical values. The closeness of the agreements with the theoretical values with soils from certain areas, on the other hand, is impressive.

The results obtained with another group of soils from near Upperville, Virginia, appear in table 2. Again it is evident that the buffer procedure indicated lime requirements deviating more than 1,000 pounds per acre from the theoretical values, although in a single instance, the agreement was within 600 pounds.

A similar comparative study of the lime requirements of a group of soil samples collected in the vicinity of Stanley, Kansas, yielded the data presented in table 3. The buffer procedure yielded conspicuously low values. In most instances this procedure gave values less than one-half, and in several instances less than one-third, the magnitude of the theoretical values.

The data assembled in table 4 indicate the results obtained from six samples obtained near Athens, Georgia. Again, the lime requirements obtained by the use of the buffer did not agree within acceptable limits with the theoretical values.

Ten samples of soils were obtained from the vicinity of Richmond, Missouri, and their lime requirements are indicated by the data appearing in table 5. The results differ markedly from those obtained with soils from the other areas studied. In all except a single instance, the buffer procedure indicated lime requirements agreeing satisfactorily in magnitude with those based on base exchange data.

TABLE 1. *Comparison of the lime requirements of soils as determined by base exchange data and by the buffer.*

LOCATION	pH	LIME REQUIREMENTS		
		By base exchange data Lbs. per acre	By buffer	
			Lbs. per acre	Deviation from theoretical value
Unsatisfactory Agreement				
Upperville, Virginia	7.20	3500	1000	2500
" "	5.80	7000	4000	3000
" "	6.15	5100	3500	1600
" "	7.05	4600	1000	3600
" "	7.10	5700	2000	3700
" "	6.05	8600	3500	5100
" "	6.50	9700	3000	6700
" "	6.70	5000	2500	2500
" "	6.85	4500	2000	2500
" "	6.65	4300	2000	2300
" "	6.95	6700	2000	4700
" "	6.80	5900	2000	3900
" "	6.85	3900	1500	2400
" "	6.05	6000	3500	2500
" "	6.40	6400	3000	3400
" "	5.90	6400	4000	2400
Satisfactory Agreement				
Athens, Georgia	5.60	4300	4000	300
" "	5.45	4900	4500	400
" "	5.5	4900	4000	900
Richmond, Missouri	5.3	4800	5000	200
Lake View, Kansas	6.5	900	1500	600
Westchester, Penn	5.7	5200	4500	700
" "	5.2	5300	5000	300
" "	5.4	5900	5000	900
" "	5.4	4800	5000	200
" "	5.6	4500	5000	500
" "	5.6	6600	6000	600

TABLE 2. *Comparison of lime requirements of soils from near Upperville, Virginia, as determined by base exchange data and by the buffer.*

pH	LIME REQUIREMENTS		
	By base exchange data Lbs. per acre	By Buffer	
		Lbs. per acre	Deviation from theoretical value
7.15	3400	1500	1900
7.05	5000	1500	3500
6.95	4500	1500	3000
6.75	4000	2000	2000
7.30	3400	1500	1900
6.60	6700	2500	4200
6.95	3400	2000	1400
7.10	2600	1000	1600
6.80	3800	2000	1800
6.10	5800	3000	2800
6.35	4000	2500	1500
7.10	3100	1000	2100
6.30	3900	2500	1400
6.70	4300	2000	2300
6.60	4600	2500	2100
6.75	2100	1500	600
7.15	2800	1500	1300
6.70	4200	2000	2200
6.20	3500	2000	1500
6.90	5500	2000	3500
7.10	3000	1500	1500
6.90	4900	2000	2900
6.10	7500	3000	4500
5.90	5600	3000	2600
6.75	3900	1500	2400
6.90	4900	2000	2900
6.40	6000	3000	3000
6.15	7000	4000	3000
6.40	5400	4000	1400
6.80	3900	2500	1400
7.20	4400	1500	2900
5.60	11,200	5000	6200
6.95	4000	1500	2500
6.45	6400	3500	2900
6.40	6500	3000	3500
6.20	9100	3500	5600
6.40	5400	3000	2400
6.70	6000	3000	3000
6.50	4500	2500	2000

TABLE 3. *Comparison of lime requirements of soils from near Stanley, Kansas, as determined by base exchange data, and by the buffer.*

pH	LIME REQUIREMENTS		
	By base exchange data Lbs. per acre	By buffer	
		Lbs. per acre	Deviation from theoretical value
6.40	4700	1500	3200
6.30	5600	2000	3600
5.85	8000	2500	5500
5.75	7400	3000	4400
6.15	6500	2000	4500
6.05	5900	2500	3400
5.50	8400	4000	4400
5.55	8100	4000	4100
5.75	7100	4000	3100
5.75	7200	3500	3700
6.20	7000	2500	4500
6.10	7600	2500	5100

TABLE 4. *Comparison of lime requirements of soils from near Athens, Georgia, as determined by base exchange data and by the buffer.*

pH	LIME REQUIREMENTS		
	By base exchange data Lbs. per acre	By buffer	
		Lbs. per acre	Deviation from theoretical value
5.50	6700	4000	2700
5.65	6800	4000	2800
5.65	5900	4000	1900
5.70	5000	4000	1000
5.75	5600	4000	1600
5.20	6400	5000	1400

TABLE 5. *Comparison of lime requirements of soils from near Richmond, Missouri, as determined by base exchange data and by the buffer.*

pH	Lime Requirements		
	By base exchange data Lbs. per acre	By buffer	
		Lbs. per acre	Deviation from theoretical value
6.50	3300	2500	800
6.65	2500	2000	500
6.35	3100	3000	100
6.85	1600	1000	600
6.90	400	500	100
5.50	5900	4000	1900
5.60	4500	4000	500
5.70	4500	4000	500
5.70	4200	4000	200
5.60	6500	5500	1000

IV. DISCUSSION

The results of the comparative study of the lime requirements from various areas as determined by base exchange data and by extraction with a buffer composed of magnesium oxide, calcium acetate, and para-nitrophenol clearly showed that the buffer procedure consistently yielded erroneous data with most soils. However in some areas, acceptable data were obtained with some samples, while in other areas, satisfactory results were the rule.

Obviously, a usable routine laboratory procedure for determining the lime requirements of soils must yield satisfactory data when applied to soils of various types and from different localities. Woodruff, himself, emphasized the necessity for any buffer procedure to function properly when used with soils of various textures, different base exchange capacities, and different degrees of base saturation.

As emphasized in the Introduction, the lime requirement of a soil represents the amount of lime required per acre to neutralize the exchangeable hydrogen adsorbed on the surfaces of the soil colloids. This hydrogen must be ***removed*** from the colloidal surfaces before it may be determined quantitatively. The ions present in the buffer extracting solution do not quantitatively replace the hydrogen on the colloids under the conditions imposed by the procedure. Conse-

quently, the change in the pH value of the buffer cannot be a dependable measure of the exchangeable hydrogen in the soil. The magnitude of the error in the final estimation of the lime requirement varies widely, for hydrogen is replaced with different degrees of difficulty in different soils. The procedure is particularly unsatisfactory when soils of high lime requirements are involved.

The buffer was thoroughly tested during the present study for its pH value in the presence of various amounts of acid hydrogen, it was found to react as predicted by Woodruff. The erroneous lime requirements obtained, therefore, are not due to the inability of the buffer to respond to hydrogen ions, but rather to its inability to quantitatively release adsorbed hydrogen from the soil colloids.

The fact that the buffer procedure yielded satisfactory data in some instances does not justify its general use in view of the dependability of the titration procedure described by Bray and DeTurk (1931).

V. CONCLUSIONS

1. The lime requirements of soil samples collected from various areas of the United States were determined by precise measurements of the exchangeable hydrogen and by extraction with a buffer consisting of magnesium oxide, calcium acetate, and para-nitrophenol.

2. The buffer procedure yielded satisfactory data only with soils from certain localities. Unsatisfactory agreements with the data obtained by base exchange procedure were obtained with most soils. The magnitude of the errors of the lime requirements determined by the buffer solution were especially great when used with soils of high base exchange capacity and with those exhibiting the smaller degrees of base saturation.

3. The buffer responded correctly to free hydrogen ions. The errors of its use to determine the lime requirements of most soils was due to its failure to quantitatively remove exchangeable hydrogen from the soil colloids.

VI. LITERATURE CITED

1. **Bray, R. H.,** and **DeTurk, E. E.** Field method for lime requirements of soils. Soil Sci. **32:** 329–341. 1931.

2. **Bray, R. H.,** and **Willhite, F. M.** Determination of total replaceable bases in soils. Ind. Eng. Chem., Anal. Ed. **1:** 144. 1929.

3. **Brown, I. D.** A rapid method of determining exchangeable hydrogen and total exchangeable bases of soils. Soil Sci. **56:** 353–357. 1943.

4. **Jones, C. H.** The determination of lime requirement by the calcium acetate method. Am. Fert. **39:** (11) 28–29. 1913.

5. **Merkle, F. G.** Soil Testing. Operation, Interpretation, and Application. Penn. Agr. Exp. Sta., Bul. **398.** 1940.

6. **Schollenberger, C. J.,** and **Dreibelbis, F. R.** Analytical methods in base exchange investigations in soils. Soil Sci. **30:** 161–173. 1930.

7. **Woodruff, C. M.** Determination of the exchangeable hydrogen and lime requirement of the soil by means of the glass electrode and a buffered solution. Soil Sci. Soc. Amer., Proc. **12**: 141–142. 1947.

8. **Woodruff, C. M.** Testing soils for lime requirement by means of a buffered solution and the glass electrode. Soil Sci. **66**: 53–63. 1948.